VOL. XI. [JANUARY, 1889.] NO. 1.

AMERICAN

CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of Purdue University, La Fayette, Indiana.

ON TAUTOMERIC COMPOUNDS.

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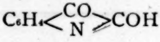
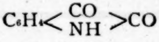
I.

There are a number of organic substances the chemical behavior of which necessitates the assumption of so-called pseudo-forms; thus, for example, carbostyril, pyridon, isatine, phloroglucin,[1] all show a twofold nature, and in order to explain this it is necessary to assume the migration of a hydrogen atom to an adjacent nitrogen or carbon atom:



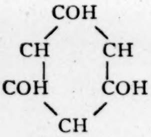
$C_6H_4<\begin{matrix}CO\\N\end{matrix}>COH$

Isatine.

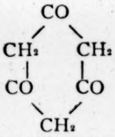


$C_6H_4<\begin{matrix}CO\\NH\end{matrix}>CO$

Pseudo-isatine.



Phloroglucin.



Pseudo-phloroglucin.

Now, as the above named compounds exist in *only one* physical modification, it is customary to explain their twofold chemical behavior as follows: it is assumed that these substances possess a so-called "mobile" or "pseudo" modification which can only be proved to exist by means of chemical reactions, and which under ordinary circumstances is incapable of existence. Thus the formation of a trioxime of phloroglucin necessitates the assumption of a pseudo-form, , as a phenol does not react with hydroxylamine. Substances which exhibit such a twofold chemical behavior are called tautomeric.

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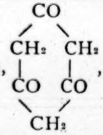
[1] Von Baeyer, Ber. d. chem. Gesell. **19**, 159.



Very recently Hantzsch and Herrmann[1] have assumed the existence of tautomerism in certain so-called quinone-hydro derivatives. They base their conclusions on purely physical grounds. A number of these compounds possess a notable di- or tri-morphism. Ethyl *p*-dihydroxy-terephthalate, for example, can be obtained in three different physical modifications, and it was very natural to suppose that these modifications might correspond to chemically different molecules—that one modification corresponds to the real dihydroxy-terephthalate, while the other two might correspond to two isomeric diketo-tetrahydro-terephthalates, thus:

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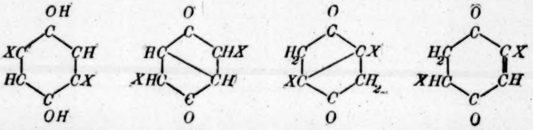

Ethyl para-dihydroxy-terephthalate (mobile modification).

(stable modification)

(mobile modification)

(modification not yet discovered)

Isomeric ethyl diketo-tetrahydro-terephthalates.

Dr. W. Muthmann[2] noticed during the Easter vacation of 1887, a very remarkable dimorphism in the analogous constituted ethyl dihydroxy-pyromellithate. This substance crystallises out of pure carbon disulphide or dry ether in greenish-yellow needles (mpt. 133.2–133.6), and pale yellow plates (mpt. 128.5°), which can be readily separated mechanically. On dissolving either modification in ether or carbon disulphide, the mixture of the two modifications is obtained again. If these are separated and the operation repeated, the same result is invariably obtained.

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[1] Ber. d. chem. Gesell. **20**, 1303, 2801; **21**, 1754.

[2] J. Chem. Soc. (London), **53**, 448-50.

The absorption spectrum of each modification dissolved in dilute sodium carbonate solution was quantitatively determined for all parts of the spectrum and found in both cases to be exactly the same. We had at that time, that is before the first publication of Hantzsch,[1] also the opinion that this dimorphism might be due to a difference in the molecular constitution of these substances; but since no chemical facts existed proving the ketone nature of ethyl dihydroxy-pyromellithate, we refrained from publishing our views on the subject.

It is certainly very noteworthy that hydroquinone, and also many derivatives of para-dihydroxy-benzene, are dimorphous. Dr. Muthmann has further observed that many para-diamido-derivatives of benzene are dimorphous, and especially also ethyl *p*-diamido-terephthalate.

Hantzsch and Herrmann have, in a series of papers,[2] assumed the chemical difference of the various modifications of ethyl *p*-dihydroxy-terephthalate; they assert that all para-dihydroxy or all benzene derivatives *must be* colorless, while ketones or quinones must be colored. The question of color is purely arbitrary and does not prove anything whatever. Heretofore more has been considered necessary in order to settle the constitution of a chemical compound.

Finally, the third (so-called "mobile") modification of ethyl *p*-dihydroxy-terephthalate is *not* colorless. Dr. Muthmann says on this subject: "I have obtained the third modification of this substance in large crystals (not good enough for a goniometric measurement). This modification is *not*, as Hantzsch and Herrmann assume and again and again state, *colorless*, but distinctly colored; in fact, *more intensely so* than ethyl succino-succinate (a substance which these chemists regard as colored). Prof. Lehmann[3] writes himself that the crystals show dichroism—pale green and colorless, while on the other hand he describes the succino-succinate as perfectly colorless."

It is not necessary to take up the remarks and assumptions of Hantzsch and Herrmann one by one and to show how little they are in accordance with the actual facts. The facts presented in this paper contradict them in many respects, so that at present I am of the opinion that the peculiar dimorphism exhibited by hydroquinone derivatives is due either to a finer isomerism, such as the relative position of the atoms of the molecule in space, or to a purely physical isomerism, *i. e.* that the molecules of the substance have a peculiar tendency to arrange themselves in two (or three) definite states of equilibrium corresponding to the totally different crystalline forms.

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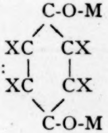
[1] Ber. d. chem. Gesell. **20**, 1303.

[2] Ibid. **20**, 1303, 2801; **21**, 1754.

[3] Zeitschr. für phys. Chemie, Heft I.

Ethyl dioxy-pyromellithate contains no double bonds, and therefore shows the characteristics of a benzene derivative. A solution of the substance in chloroform, even if allowed to stand for days, is not acted upon by an excess of bromine. The assumption of para-bonds by Hantzsch and Herrmann (see page 2, formulæ I and II) is purely arbitrary. According to the wonderful investigation of Von Baeyer on hydrated phthalic acids,[1] there is no tendency to form compounds having para-bonds. Finally, such tetrahydrated compounds, if they do exist, would surely form with bromine stable addition-products. The red-colored salts of ethyl dioxy-pyromellithate have the metal undoubtedly bound to oxygen, thus:  . The salts of this undoubted benzene-derivative are therefore *not colorless*, but deep red in color. A comparative (not yet completed) study of the salts of phenols has already shown the remarkable resemblance of these salts to one another and to the salts of ethyl aceto-acetate.

The only chemical evidence that Hantzsch and Herrmann have to offer for the tautomerism of hydroquinone compounds is the fact that ethyl tetra-oxy-terephthalate and ethyl quinone-dioxy-terephthalate form dioximes[2] with hydroxylamine. The peculiar method of formation of these substances makes it little probable that they are actually dioximes. From the experience that I have gained from the study of nitranilic acid (see following paper), there is good reason for believing that these so-called dioximes are nothing else than oxyammonium salts. The analyses of Loewy are also in favor of this conclusion. By the action of hydroxylamine chlorhydrate in excess on ethyl quinone-dioxy-terephthalate, Loewy[1] obtained a substance which he regarded as a mixture of monoxime and of dioxime, because it gave too low but constant figures on analysis:

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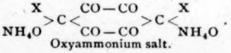
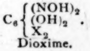
[1] Ann. Chem. (Liebig) **245**, 103.

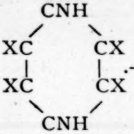
[2] Hantzsch and Zeckendorf, Ber. d. chem. Gesell. **20**, 2799, 2800.

	Calculated for  ${}^{X}_{NH_4O}{>}C{<}^{CO-CO}_{CO-CO}{>}C{<}^{X}_{NH_4O}$. Oxyammonium salt.	Calculated for  $C_6\begin{cases}(NOH)_2\\(OH)_2\\X_2\end{cases}$. Dioxime.
N	7.65	8.9

Loewy found 7.47, 7.58 and 7.83 per cent.

Although ethyl dioxy-pyromellithate reacts under no condition with hydroxylamine, ammonia, or ammonic acetate, it readily forms with phenylhydrazine a dipyrazolon derivative. This is, up to the present time, the only proof (chemical) that exists for the tautomerism of hydroquinone derivatives, and I do not regard it as final until the intermediary product, the dihydrazide, is isolated, as has been done in the case of ethyl succino-succinate.[2]

EXPERIMENTAL PART.

Ethyl quinone-di-imido-tetracarboxylate or ethyl quinone-di-imido-pyromellithate,  .—On adding bromine (1.8 gram dissolved in 10 grams chloroform) to a cooled solution of 2 grams ethyl diamido-pyromellithate, and allowing the mixture to stand over night, colorless needles separate out in large quantity. After allowing the chloroform to evaporate spontaneously, there remains a yellow oil, which dissolves without decomposition in alcohol, and which is either the hydrobromic acid salt or a hydrobromic acid addition-product of the above named quinone-di-imide. On adding water and rubbing with a glass rod, the oil is transformed into a solid yellow substance, while hydrobromic acid is found in the aqueous solution in large amount. On crystallising the yellow product from alcohol, it is obtained in long orange-yellow prisms, or also in radiating orange-yellow needles, melting at 161°.

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[1] Ber. d. chem. Gesell. **19**, 2394.

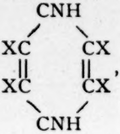
[2] Knorr, Ibid. **17**, 2055.

0.2398 gram substance dried at 110° gave 0.1257 gram H_2O and 0.4795 gram CO_2.

	Calculated for $C_6\begin{cases}(NH)_2\\(CO_2C_2H_5)_4\end{cases}$	Found.
C	54.82	54.50
H	5.58	5.83

The quinone-di-imide is volatile without decomposition, and dissolves readily with pure yellow color, and without fluorescence, in chloroform, benzene, and hot alcohol. The alcoholic solution gives no coloration with ferric chloride. Zinc dust and acetic acid reduce the substance with ease to ethyl diamido-pyromellithate. The relation between these two substances is therefore similar to that which exists between quinone and hydroquinone.

The stability of the quinone-di-imide group is noteworthy; it has not been found possible in any way to convert the compound into the corresponding quinone. On dissolving it in concentrated sulphuric acid, adding a little water and heating, it remains in great part unchanged. Benzene does not extract it from a concentrated sulphuric acid solution, so that it must possess slight basic properties. Concentrated hydrochloric acid or potassium hydrate has no action on the substance. The action of concentrated nitric acid is also noteworthy. The compound dissolves therein with a dark violet color, which after a little while changes to a yellow color. On the addition of water a yellow oil is precipitated, which is insoluble in potassium hydrate, contains nitrogen, and is volatile without decomposition. This oil can in no way be converted back to the quinone-di-imide or to the diamido-compound.

In order to find out whether the quinone-di-imide possesses double bonds, , it was treated in chloroform solution with two molecules of bromine. After standing for two days, very little change was noticed. On allowing the mixture to stand for two days longer, I noticed, besides unchanged quinone-di-imide, a substance which is much more readily soluble in alcohol, and which crystallises therefrom in pale yellow large plates melting at 85°. The compound contains no bromine; it contains nitrogen, and is volatile easily without decomposition. It cannot be converted back into the quinone-di-imide or the diamido-compound. As soon as more material is at my disposal it will be thoroughly investigated. The above facts prove at all events that the quinone-di-imide contains no double bonds.

In order to obtain the material from ethyl diamido-pyromellithate for the study of the following compounds, it was found that the conversion of this substance into ethyl *p*-diketo-hexamethylene-tetracarboxylate by means of zinc dust, alcohol and dilute sulphuric acid (1 : 3), gave by far the best yield. In this way the diketo-compound was obtained mixed with 30–70 per cent. of the di-imide. The substances resemble one another very closely, are colorless, and have very nearly the same fusing point. On treating the mixture with bromine, beautiful orange-red mixed crystals (melting point 131°) of ethyl diamido- and dioxy-pyromellithate were obtained. The same mixed crystals were obtained by crystallising equal parts of these two substances from alcohol.

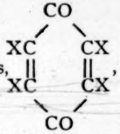
The di-imide loses its nitrogen very readily, and it is only necessary to dissolve the above mixture in concentrated sulphuric acid, to add a little water, and after standing for twenty minutes, to precipitate completely with more water. On treating the pure diketo-compound thus obtained with bromine in chloroform solution, it is converted quantitatively into ethyl dioxy-pyromellithate.

Action of Various reagents on Ethyl Quinone-tetracarboxylate.

1. *Phenylhydrazine.* On treating an alcoholic solution in the cold with phenylhydrazine, a violent evolution of gas (nitrogen) immediately takes place, and the quinone is reduced to the hydroquinone. Exactly the same reaction took place on working with an acetic acid solution.

2. *Hydroxylamine.* On adding hydroxylamine hydrochloride to an alcoholic solution in the cold, the quinone is instantly reduced to the hydroquinone. The same result is obtained with a neutral hydroxylamine solution.

3. *Ammonia.* An alcoholic ammonia solution of the quinone is reduced to the hydroquinone on warming.

4. *Bromine.* If the quinone contains double bonds,  it must form an addition-product with bromine—which it does not. One gram quinone was allowed to remain four days in chloroform solution with four molecules bromine. After the spontaneous evaporation of the chloroform (over sulphuric acid in a vacuum), there remained a product which crystallised from alcohol in greenish-yellow needles (melting point 133°), which proved to be nothing but the hydroquinone. 0.3 gram of pure hydroquinone was thus obtained; bromine therefore manifestly decomposes a part of the quinone, with the formation of the hydroquinone. If the quinone is allowed to stand in chloroform solution with bromine for a short time, one finds, besides the hydroquinone, much unchanged quinone.

These facts, as well as the observed transformation on saponification with alkalies or acids, prove the extraordinary tendency of quinone derivatives to pass over into the corresponding hydroquinone.

Action of Various Reagents on Ethyl Hydroquinone-tetracarboxylate.

1. *Hydroxylamine.* The hydroquinone dissolved in alcohol is not acted upon by hydroxylamine hydrochloride in excess, whether heated in a sealed tube at 130°–140° for six to eight hours, or allowed to stand in the cold for a week. From an alkaline solution, hydroxylamine hydrochloride precipitates the hydroquinone. This reaction will be explained clearly later. A neutral solution of hydroxylamine does not react on an alcoholic solution of the substance, whether heated in a sealed tube at 100° or allowed to stand for five days.

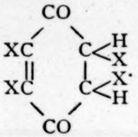
2. *Phenylhydrazine.* Although phenylhydrazine does not react in acetic acid solution, even if heated for a long time in a sealed tube at 130°, it does react very readily and completely on heating an alcoholic solution of the hydroquinone in a sealed tube at 100° for six hours. After distilling off the alcohol, the dark-brown residue was dissolved in acetic acid and precipitated in

reddish-yellow flakes by adding water. These were washed with ether, then dissolved in dilute sodium hydrate; the filtered solution thereupon poured slowly into dilute sulphuric acid, and thus the substance again precipitated in yellow flakes. For analysis it was crystallised from a large amount of pure ether, and obtained in yellow flakes.

0.0745 gram substance gave 8 cc. nitrogen at 28° and 747 mm. barom.

	Calculated for $C_6H_2\left\{\begin{matrix}(CO_2C_2H_5)_2\\(N_2COC_6H_5)_2\end{matrix}\right.$.	Found.
N	11.52	11.96

The substance possesses the properties of a dipyrazolon-derivative. It dissolves in alkalies with purplish-red color and yellow fluorescence. The alcoholic solution gives with ferric chloride a dark-red coloration. It dissolves readily in alcohol, very difficultly in ether and benzene. It is soluble in concentrated sulphuric acid, and is precipitated therefrom by water in yellow flakes. On heating, it chars at a high temperature without melting. Since it can contain no unchanged CH_2 group, it gives with nitrites no pyrazolblue[1] compound. The formation of this dipyrazolon derivative seems to prove the tautomeric nature of the hydroquinone, and we are compelled to assume the existence of a pseudo-form,



Up to the present time I have not succeeded in obtaining the dihydrazide which contains 9.5 per cent. nitrogen.

3. *Bromine.* The hydroquinone compound treated in chloroform solution with bromine in excess remains unchanged, even though allowed to stand for six days. It can therefore contain no double bonds, but reacts like a benzene derivative. The existence of a pseudo-form—a diketo-tetra-hydro-benzene compound—under ordinary circumstances is in a high degree improbable.

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[1] Knorr, Ber. d. chem. Gesells. **17**, 551, 2055.

Experiments to determine whether the Metal in the Salts of Ethyl Hydroquinone-tetracarboxylate is bound to Oxygen or to Carbon.

Isolation of the sodium salt, $C_6\left\{\begin{matrix}O_2\\Na_2\\(CO_2C_2H_5)_4\end{matrix}\right.$.—A benzene solution of ethyl hydroquinone-tetracarboxylate (1 mol.) is added slowly to a solution of 2 molecules sodium ethylate in benzene (dried over sodium). The sodium salt separates out as a gelatinous, almost invisible, red precipitate. After filtration it was put on clay plates and washed with benzene, and finally dried at 100°. It forms, thus, a deep red granular product.

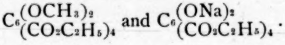
0.1374 gram substance gave 0.0445 gram sodium sulphate.

	Calculated for $C_6\left\{\begin{matrix}Na_2\\O_2\\(CO_2C_2H_5)_4\end{matrix}\right.$.	Found.
Na	10.41	10.49

When dry the salt is perfectly stable; it chars at a high temperature. An aqueous solution gives yellow flaky precipitates with barium chloride, lead acetate, and copper sulphate. A silver nitrate solution is instantly reduced in the cold. Hydroxylamine hydrochloride precipitates directly ethyl hydroquinone-tetracarboxylate, forming sodium chloride and free hydroxylamine. The dry salt brought in contact with the vapor of acetyl chloride is instantly converted, with marked evolution of heat, into sodium chloride and the diacetyl derivative of the hydroquinone which is described below. Heated with alcohol, in which it is little soluble, and methyl iodide, it is converted into sodium iodide and the dimethoxy-derivative which is described below. On adding bromine water to an aqueous solution of the salt, ethyl quinone-tetracarboxylate is formed according to the equation,

$$C_6\left\{\begin{matrix}Na_2\\O_2\\(CO_2C_2H_5)_4\end{matrix}\right. + Br_2 = C_6\left\{\begin{matrix}O_2\\(CO_2C_2H_5)_4\end{matrix}\right. + 2NaBr.$$

This is a new method for making quinones, which promises success where other methods fail. It is not necessary to isolate the sodium salt. The hydroquinone is dissolved in the calculated amount of sodium hydrate, and the calculated amount of bromine water quickly added. Treated in this manner, ethyl dioxyterephthalate is changed: it was not possible, however, because of the small amount of substance at my disposal, to prove whether thus the long-sought-for ethyl quinone-terephthalate was actually formed. On replacing the sodium atoms in the salt of ethyl hydroquinone-tetracarboxylate with methyl, there is formed a dimethoxy-derivative which is not in the least acted upon by bromine, and which does not, under any conditions, react either with hydroxylamine or with phenylhydrazine. Thereby it is proved that the methyl groups, and hence also the sodium atoms, are bound to oxygen, as represented in these formulæ:



$$C_6\begin{matrix}(OCH_3)_2\\(CO_2C_2H_5)_4\end{matrix} \text{ and } C_6\begin{matrix}(ONa)_2\\(CO_2C_2H_5)_4\end{matrix}.$$

It is noteworthy that as soon as the metal or the hydrogen atoms in the hydroquinone are replaced by methyl or by acetyl, the products formed are perfectly colorless, show no fluorescence in solution, and give no coloration with ferric chloride. These facts are in harmony with those observed in the case of other phenols, as well as in the case of di-substituted aceto-acetic ethers.

On comparing the above reactions of ethyl disodic-hydroquinone-tetracarboxylate with those of sodium aceto-acetic ether, one cannot fail to be astonished at the great resemblance in their behavior. It is therefore also probable that in the last named compound the sodium is bound to oxygen, $CH_3-CONa=CH-CO_2C_2H_5$.

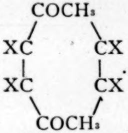
Finally, I have made the salts of a whole series of phenols, which on account of their instability have been little studied, the subject of a detailed investigation. The facts already obtained prove the great resemblance in chemical behavior of all these salts with those above mentioned. The sodium salt of hydroquinone was obtained, by means of sodium ethylate and dry ether, as a flaky white precipitate which, when moist, is extremely unstable and turns deep blue in color; when dry, however, it is tolerably stable. This salt gives reactions entirely analogous to those obtained with ethyl sodic-hydroquinone-tetracarboxylate. Hydroxylamine hydrochloride sets hydroquinone free; bromine gives quinone; acetyl chloride gives diacetyl-hydroquinone; silver nitrate is instantly reduced.

The sodium salt of tetrachlor-hydroquinone, $C_6Cl_4(\overset{1.4}{OH})_2$, was obtained in colorless flakes which, when moist, quickly turn green. With the reagents used with hydroquinone, it gives entirely analogous reactions.

The sodium salt of resorcin, $C_6H_4(\overset{1.3}{OH})_2$, was obtained in colorless flakes. These deliquesce on heating at 100° and become viscous. The salt gives completely analogous reactions with the above reagents. Of some interest is the product, free from bromine, obtained by treating the sodium salt with bromine water.

The facts which are at present known about salts which have the metal bound directly to the carbon-atom, *e. g.* the salts of the nitro-derivatives of the fatty series (Victor Meyer), show that the metal is more firmly bound and can be replaced by bromine. The silver salts are stable, and many salts are not decomposed even by mineral acids. The metal cannot be replaced by the methyl or acetyl group.

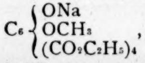
Ethyl Dimethoxy-hydroquinone-tetracarboxylate,



This compound is formed by treating the sodium salt with methyl iodide. It was made, just as in the case of the alkyl derivatives of aceto-acetic ether, in the following manner :

2 molecules of sodium were dissolved in alcohol, and, after cooling, an alcoholic solution of the hydroquinone (1 molecule) was added; thereto a little more than 2 molecules of methyl iodide were added, and the mixture heated on a water-bath, with reversed condenser, for six hours.

There is formed at first an intermediary product which crystallises from alcohol in large yellow plates. This is undoubtedly



$$C_6\begin{cases} ONa \\ OCH_3 \\ (CO_2C_2H_5)_4 \end{cases}$$

, as it is readily converted by heating with methyl iodide into the dimethoxy-derivative. After distilling off the alcohol, water was added and the emulsion extracted with ether. The ethereal solution, after being washed with dilute sodium hydrate, left on evaporation a colorless product, which on recrystallisation from dilute alcohol was obtained in colorless needles, melting at 95°.

0.1261 gram substance dried in a vacuum gave 0.0722 gram H_2O and 0.2577 gram CO_2.

	Calculated for $C_6\left\{\begin{matrix}(OCH_3)_2\\(CO_2C_2H_5)_4\end{matrix}\right.$.	Found.
C	56.34	55.74
H	6.10	6.36

The compound is colorless, volatile without decomposition, and easily soluble in organic solvents. The solutions show no fluorescence or coloration with ferric chloride. A chloroform solution allowed to stand for 3 days with an excess of bromine was not affected. The substance, therefore, is a benzene derivative, and not a keto-tetra-hydro-benzene derivative. This is still further confirmed by the fact that it does not undergo the slightest change when heated in a sealed tube at 100° with hydroxylamine or with phenylhydrazine.

An alcoholic solution of the substance treated with zinc dust and hydrochloric acid takes up hydrogen, just as the corresponding hydroquinone; there is formed a colorless oil, insoluble in sodium hydrate. The oil could not be made to solidify, but, treated with bromine in chloroform solution, it is converted back again to the original substance, with evolution of hydrobromic acid.

Ethyl Diacetyl-hydroquinone-tetra-carboxylate, $C_6\left\{\begin{matrix}(OCOCH_3)_2\\(CO_2C_2H_5)_4\end{matrix}\right.$.

This compound is formed by the action of acetyl chloride on the dry sodium salt. The reaction takes place instantly in the cold, with marked evolution of heat. After the acetyl chloride has evaporated, the residue is washed with dilute sodium hydrate, and then crystallised from alcohol. The acetyl compound is thus obtained in colorless plates melting at 120°.

0.1222 gram substance (dried at 100°) gave 0.0640 gram H_2O and 0.2432 gram CO_2.

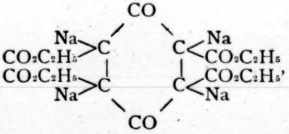
	Calculated for $C_6\left\{\begin{matrix}(OCOCH_3)_2\\(CO_2C_2H_5)_4\end{matrix}\right.$.	Found.
C	54.76	54.28
H	5.40	5.82

The substance is colorless, volatile without decomposition, insoluble in alkalies. It is not acted upon by bromine in chloroform solution.

The solutions show no fluorescence nor coloration with ferric chloride.

Experiments to determine whether the Metal in the Salts of Ethyl p-Diketo-hexamethylene-tetra-carboxylate is bound to Oxygen or to Carbon.

In the first place, the question whether a tetra-sodium salt can be formed had to be settled. It is evident that if the sodium is bound directly to carbon, the following salt,



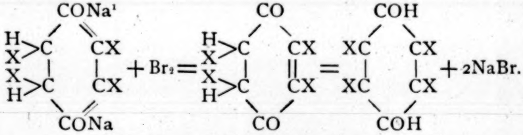
could be formed. As a matter of fact, however, such a salt does not exist. A benzene solution of the diketo compound, even when treated with a large excess of sodium ethylate, gives only a di-sodium salt. To obtain this di-sodium salt, exactly the same method was employed as in the case of the corresponding hydroquinone. It was obtained as a pale rose-colored, almost invisible, very gelatinous precipitate which it is exceedingly difficult to filter. It was therefore found advantageous to put the salt on porous clay plates and wash it with benzene. After drying at 100° and again washing with benzene, it formed, dried at 100°, a scaly, pale rose-colored product.

0.1285 gram substance gave 0.0425 gram sodium sulphate.

	Calculated for $C_6\left\{\begin{matrix}H_2\\Na_2\\O_2\\(CO_2C_2H_5)_4.\end{matrix}\right.$	Found.
Na	10.36	10.71

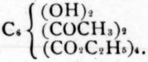
The salt shows in every respect similar reactions to that of the corresponding hydroquinone. An aqueous solution gives pale yellow flaky precipitates with lead acetate and copper sulphate. A silver-nitrate solution is instantly reduced. Hydroxylamine hydrochloride sets free the diketo compound; acetyl chloride forms instantly a diacetyl-derivative. The alkyl iodides react, forming alcohol ethers, which have not yet been analysed. Treated with bromine water, ethyl hydroquinone-tetra-carboxylate is formed. The compound obtained thus is identical with the one obtained by reduction of the quinone, and possesses the same peculiar dimorphism.

This is a new method for converting the diketo compound, as well as ethyl succino-succinate, into ethyl hydroquinone-tetra- or para-di-carboxylate. Naturally it is not necessary to isolate the sodium salt. The reaction, it seems to me at present, can be explained as follows:



Hypothetical intermediary product, not capable of existence under ordinary circumstances (pseudo-form).

Ethyl Diacetyl-p-diketo-hexamethylene-tetracarboxylate,



$$C_6\begin{cases}(OH)_2\\(COCH_3)_2\\(CO_2C_2H_5)_4.\end{cases}$$

This substance was made in exactly the same way as the corresponding compound of the hydroquinone, except that it was not treated with sodium hydrate. Crystallised from alcohol it forms colorless needles melting at 142°.

0.1050 gram substance dried at 110° gave 0.0580 gram H_2O and 0.2080 gram CO_2.

	Calculated for $C_6\begin{cases}(OH)_2\\(COCH_3)_2\\(CO_2C_2H_5)_4.\end{cases}$	Found.
C	54.55	54.29
H	5.79	6.14

This compound possesses entirely unexpected properties. It gives a blood-red coloration with ferric chloride. It dissolves in dilute sodium hydrate and sodium carbonate solution, in the cold, much more readily than the diketo compound. The sodium salt obtained in the ordinary way with sodium ethylate and benzene, is pale rose-colored, and very much less gelatinous than the diketo salt. The salt gives reactions entirely analogous to those given by salts of phenols. Bromine water gives a product containing no bromine, and melting at about 155°, which, therefore, cannot be the diacetyl derivative of the hydroquinone. Acetyl chloride gives an acetyl derivative instantly, which has not been further studied. A silver-nitrate solution is at once reduced in the cold. These facts can only be explained on the supposition that a molecular rearrangement has taken place, like that which in all probability takes place when sodium aceto-acetic ether is treated with alkyl iodides or acetyl chloride:

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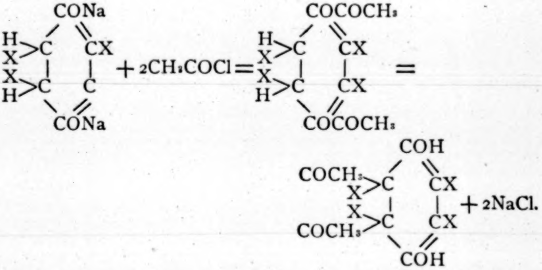
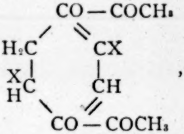
[1] One of 3 possible formulæ, as para-bonds can also be assumed. If, however, as is probable, the hydroquinone is hydrated, like the phthalic acids [Ann. Chem. (Liebig) **245**, 103], the two hydrogen atoms must be on adjacent carbon atoms.



It is noteworthy that the diacetyl derivative of ethyl succino-succinate, according to Wedel,[1] is insoluble in cold sodium hydrate.

It must therefore possess the formula,



, and, if so, it must be possible to convert the substance, by means of bromine, into the diacetyl derivative of the ethyl *p*-dioxy-terephthalate.

The alcohol ethers of the diketo compound are readily formed by means of sodium ethylate and alkyl iodides. Only viscous products have as yet been obtained, and these are partly soluble and partly insoluble in sodium hydrate. Since the methylated products cannot in any way be converted into the known dimethoxy derivative of the hydroquinone, it is not improbable that a similar molecular rearrangement has taken place in this case also.

These compounds will be thoroughly investigated as soon as

[1] Ann. Chem. (Liebig) **219**, 86.

possible. Since the preparation of the material from durylic acid is an extremely tedious operation, the progress must be somewhat slow.

THE CONSTITUTION OF THE ANILIC ACIDS.

By J. U. Nef.

I.

In a previous paper[1] I have shown that nitranilic acid salts can be obtained by the action of nitrites on chloranil. The following method is now employed in the production of sodium nitranilate: 10 grams of finely pulverised chloranil are put into a flask and moistened thoroughly with alcohol. A concentrated solution of 20 grams sodium nitrite is then added, and the mixture heated; gently, at first, until the violent reaction has subsided, and finally on a water-bath for four to six hours. The residue is dissolved in hot water, and filtered from some unchanged chloranil. On cooling, sodium nitranilate separates out in great part from the filtrate. The yield is from 60–70 per cent.

Sodium nitranilate is not the sole product formed by the action of the nitrite on chloranil. There are formed sodium salts of several other acids, which are much more readily soluble in water, and therefore can easily be separated from sodium nitranilate. Especially noticeable is an apparently homogeneous sodium salt, crystallising in red needles, which, however, after repeated crystallisation gave no constant figures on analysis. Further study has proved that this substance is a mixture of salts of two, possibly three, different acids. A full treatise on these compounds, as well as on the replacement of the chlorine atoms in chloranil by various other radicals, will appear in this journal as soon as the work is completed.

As regards the sodium and potassium nitranilate from chloranil, Dr. W. Muthmann has confirmed, by comparison, the absolute physical identity with the products[2] obtained from hydroquinone. The octahedra of sodium nitranilate from pure chloranil possess a marked dichroism—reddish yellow and deep brownish red, while those from hydroquinone are pure yellow in color and possess no dichroism. The product from chloranil is rendered impure by a trace of foreign matter, which is very difficult to eliminate by repeated crystallisation.

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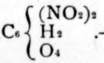
[1] Ber. d. chem. Gesell. **20**, 2027.

[2] Kindly sent to me by Dr. R. Nietzki for comparison.

By converting the salt into the free acid, however (see below), and afterwards treating with sodium hydrate, the sodium salt is also obtained in pure yellow octahedra showing no dichroism.

Nitranilic Acid,  $C_6\left\{\begin{array}{l}(NO_2)_2\\ H_2\\ O_4\end{array}\right.$.—This substance (containing water of crystallisation) Nietzki[1] has already had in his hands, but on account of its instability it was not analysed. The following method was pursued in isolating the acid: 10 grams very finely pulverised sodium nitranilate (dried at 150°) were slowly added to 40 cc. concentrated nitric acid (sp. gr. 1.4, cooled to 0°). After allowing to stand for several hours, an equal volume of water was added, taking care to keep the temperature at 0° or below. The free acid separates out in yellow needles. It was filtered off, put on porous clay plates, and when dry, redissolved in a small amount of water, and separated from some unchanged sodium salt. To the filtrate one third its volume of concentrated nitric acid is added, keeping the solution at 0° or below. The acid crystallises out in needles, is filtered off, dried on clay plates, and finally allowed to stand for two days over sulphuric acid in a vacuum.

I. 0.1590 gram substance, dried at 100°, gave 0.0188 gram H_2O and 0.1804 gram CO_2.

II. 0.1945 gram substance, dried at 100°, gave 0.0252 gram H_2O and 0.2221 gram CO_2.

III. 0.1600 gram substance, dried at 100°, gave 17 cc. N_2 at 18° and 749 mm.

	Calculated for $C_6N_2O_8H_2$.	Found.	
		I. From $C_6N_2O_8Na_2$.	II. From $C_6N_4O_{10}H_8$.
C	31.31	30.95	31.14
H	.87	1.31	1.44
N	12.17	12.30	...

Nitranilic acid is very readily soluble in water; less so in the presence of acids. Acetic ether extracts it from a dilute sulphuric acid solution, but not from an aqueous solution. The acid is soluble in organic solvents without decomposition. From acetic ether it was obtained in clear, glistening yellow prisms. An aqueous solution of the acid decomposes very quickly on warming, with liberation of prussic acid, and formation of an organic acid giving a yellow barium salt. The same reaction takes place, only more slowly, in the cold. The pure dry substance, however, can be kept for months without undergoing the slightest decomposition. On heating, it explodes without melting at a high temperature.

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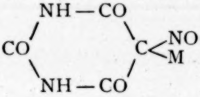
[1] Ann. Chem. (Liebig) **215**, 139.

The acid decomposes chlorides, sulphates, and nitrates, forming nitranilates and free hydrochloric, sulphuric, or nitric acid.

Treated with hydroxylamine hydrochloride, an oxyammonium salt separates out directly: $C_6N_2O_8H_2 + 2NH_4OCl = C_6N_4O_{10}H_8 + 2HCl$.

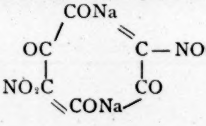
Chemical Conduct of Nitranilates.

The salts of nitranilic acid possess at ordinary temperature an extraordinary stability. They are all explosive, especially the mercuric salt. In their entire chemical and physical behavior they show a great resemblance to the salts of the nitro-derivatives of the fatty series, which undoubtedly have the metal bound directly to carbon. They also show resemblance to the salts of fulminic, barbituric, and dilituric acids. The salts of dilituric acid,



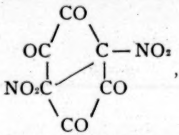
especially, are very stable, and many of them are not decomposed by mineral acids. Finally, the nitranilates show in their chemical behavior a marked difference from that shown by salts of phenols (see preceding paper). Hydroxylamine hydrochloride does not set free the acid, but forms a stable oxyammonium salt. The silver salt is very stable, and can be heated in a sealed tube at 130° for 6–8 hours with methyl iodide without change. By treating the sodium salt with bromine water, it was not found possible under any conditions to obtain a product free from bromine, but the bromine replaced the sodium atom directly.

If sodium nitranilate possesses the commonly accepted constitution,



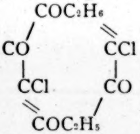
, it is difficult to see why, by the

action of one molecule bromine, a compound of the formula,


CO
OC
C—NO₂
NO₂C
CO
CO

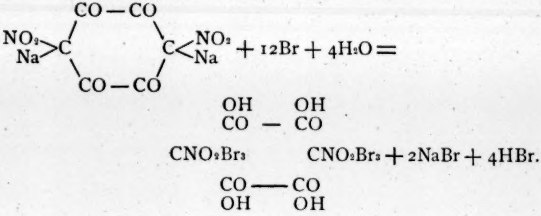
, cannot be formed. Such a reaction would be entirely analogous to that noticed by myself in the case of the sodium salts of ethyl *p*-diketo-hexamethylene-tetracarboxylate and of ethyl succino-succinate (*vid.* preceding paper). The presence of negative groups cannot be the cause of the different chemical behavior, since the sodium salt of tetrachlor-hydroquinone is an unstable compound, and gives reactions entirely analogous to those given by other phenol salts.

Although it was not possible, under any conditions, to obtain alcohol ethers or an acetyl derivative of nitranilic acid, Stenhouse[1] has obtained the ethyl ether of chloranilic acid. This compound, if it has the formula


COC₂H₆
CO
CCl
CCl
CO
COC₂H₅

, must take up bromine, which as a matter of fact it does not.

On treating sodium nitranilate with 12 molecules bromine, the closed chain of six carbon atoms is quantitatively split up into oxalic acid and brompicrin, according to the equation,


CO — CO
NO₂
Na
C
C
NO₂
Na
CO — CO
+ 12Br + 4H₂O =
OH OH
CO — CO
CNO₂Br₃
CNO₂Br₃ + 2NaBr + 4HBr.
CO — CO
OH OH

This, to my knowledge, is the first observed quantitative splitting up of a closed chain of six carbon atoms into fatty compounds.

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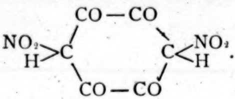
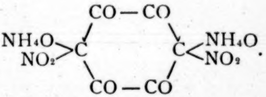
[1] J. Chem. Soc. (London), **23**, 4.

The above mentioned facts seem to me to make the following constitution of nitranilic acid probable,



It is therefore nothing but a para-dinitro-derivative of tetra-keto-hexamethylene.

Oxyammonium-nitranilate,



This substance is formed on adding hydroxylamine hydrochloride to a solution of nitranilic acid, or of sodium nitranilate (hot). In the former case it separates out as a yellow granular powder; in the latter, in long dark-yellow plates. Crystallised once from hot water it is pure.

I. 0.2130 gram substance, dried at 110° and mixed with lead chromate, gave 0.0568 gram H_2O and 0.1900 gram CO_2.

II. 0.1452 gram substance, dried at 110°, gave 0.0422 gram H_2O and 0.1287 gram CO_2.

III. 0.2080 gram substance, dried at 110°, gave 34.5 cc. N_2 at 17.5° and 757.5 mm.

	Calculated for $C_6N_4O_{10}H_8$.	Found. I. From $C_6N_2O_8Na_2$.	II. From $C_6N_2O_8H_2$.
C	24.33	24.52	24.18
H	2.69	2.96	3.23
N	18.92	19.42	...

On being heated, the substance explodes at a high temperature without melting. Obtained from sodium nitranilate, it possesses a dark-yellow color; from nitranilic acid, however, a pure yellow color. The form of the crystals is the same in both cases. The above-mentioned impurity in the case of the sodium salt, therefore, goes over into the oxyammonium salt. When added to cold concentrated nitric acid (1.4), the salt is converted into nitranilic acid (analysis above).

Noteworthy is the action of the oxyammonium salt with hydroxylamine hydrochloride. On boiling 10 grams of the salt, suspended in water, with an excess of hydroxylamine hydrochloride

(4 molecules), a violent evolution of gas (nitrogen, carbon dioxide, and some prussic acid) is noticed after a while. When the gas has ceased to come off, about 2 grams of substance crystallise out from the yellow solution on cooling, in long yellow needles. A series of analyses have proved that this compound contains the group C_6N_5 or C_5N_4. It loses one atom of nitrogen when treated with concentrated nitric acid, and is converted into a substance containing the group C_6N_4 or C_5N_3. The products obtained explode on heating; it would be premature to attempt to give them formulæ, since, in all probability, they contain water of crystallisation.

Action of Bromine on Sodium Nitranilate.

On adding a little more than the calculated amount of bromine (105 grams) to 30 grams very finely pulverised sodium nitranilate suspended in water (250 cc.) cooled to 0°, the color of the bromine rapidly disappears, with marked evolution of heat; at the same time a vapor with a powerful odor, and strongly affecting the eyes, is noticed. Finally, there is found at the bottom of the vessel a heavy oil colored yellow by bromine. After standing for half an hour, the excess of bromine is got rid of by sulphurous acid, and the oil extracted with ether. The ether is then distilled off, and the residual oil, after being heated for some time at 100°, is distilled over with steam. By means of a drop-funnel it is separated from water, and then dried with fused calcium chloride.[1] The analysis of the oil gave figures agreeing with brompicrin, with which it also coincides in all its properties.

0.4654 gram substance gave 0.0109 gram H_2O and 0.0689 gram CO_2.

0.4944 gram substance gave 23 cc. N_2 at 30° and 750 mm.

0.2537 gram substance gave, heated with CaO, 0.480 gram AgBr.

	Calculated for $C\left\{\begin{matrix}Br_3\\NO_2\end{matrix}\right.$	Found.
C	4.04	4.04
Br	80.52	80.50
N	4.72	5.17
H	...	.26

In the aqueous solution is found on evaporation, besides hydrobromic acid, nothing but oxalic acid and sodium bromide. The oxalic acid was obtained in long transparent prisms melting in their water of crystallisation at 101.5°. On standing over sulphuric acid it lost its water of crystallisation, and crumbled to a white powder, melting, with decomposition, towards 188°. An analysis of the calcium salt, dried at 110°, gave the following figures:

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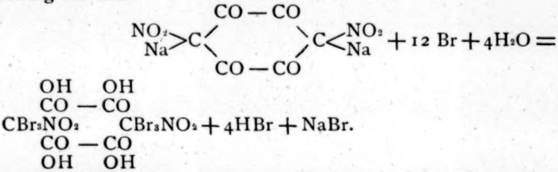
[1] Victor Meyer, Ann. Chem. (Liebig) **180**, 122.

0.2374 gram substance gave 0.2188 gram $CaSO_4$.

	Calculated for $CaC_2O_4.H_2O$.	Found.
Ca	27.4	27.11

Sodium nitranilate is therefore split up by means of bromine into brompicrin, $C{<}^{Br_3}_{NO_2}$, and oxalic acid, according to the following reaction:



A quantitative determination with 3 grams sodium nitranilate (dried at 150°) gave:

3.190 grams calcium oxalate, $CaC_2O_4.H_2O$, dried at 110°. 3.197 grams, calculated.

30 grams sodium nitranilate gave 66 grams crude $C{<}^{Br_3}_{NO_2}$, calculated 65.3 grams.

It now seemed probable that the salts of the other anilic acids could be split up in an analogous[1] manner with bromine. Experiments begun with potassium chloranilate have indeed confirmed this opinion. On treating the substance with bromine, exactly as above, I obtained a heavy colorless oil readily volatile with steam, and having an odor very much like that of chloroform. It is very probable that this substance is tribrom-chlor-methane, CBr_3Cl.[2] Besides this oil, oxalic acid is formed, but in much smaller quantity than in the case of sodium nitranilate.

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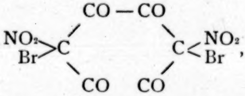
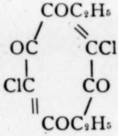
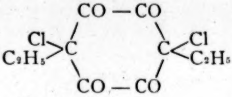
[1] The sodium salt of the so-called ethyl-quinone-dioxy-dicarboxylate can, in all probability, be split up into tribromacetic ether and oxalic acid. The free ester gives with chlorine, as is well known, ethyl tetra-chlordiketo-adipinate. Hantzsch and Zeckendorf, Ber. d. chem. Ges. **20**, 1309.

[2] Besides the oil, I obtained traces of a substance crystallising in colorless plates (mpt. 88°) which correspond with CBr_4 in properties.

Attention is called to the fact that the free anilic acids, on treatment with halogens, yield totally different products. Thus bromanilic acid gives with bromine, per-brom-acetone.[1] Chloranilic acid gives with bromine the symmetrical tetra-brom-dichlor-acetone;[2] with chlorate of potash and hydrochloric acid, tetra-chlorinated acetone and diacetyl.[3]

A number of experiments were made with the idea of obtaining from sodium nitranilate with bromine an intermediary product, such as , but without success. On treating the nitranilate with but one molecule bromine, brompicrin is formed. On the other hand, the experiments just begun with potassium chloranilate promise a better result.

Finally, attempts to obtain a methyl ether or an acetyl derivative of nitranilic acid were fruitless. While acetyl chloride is without action on the sodium salt at ordinary temperature, there is formed, on heating in a sealed tube at 100°, chloride of sodium with total decomposition of the nitranilic acid molecule. Methyl iodide does not act on the silver salt even when heated for 6–8 hours in a sealed tube at 130°. On heating at 180°–200°, decomposition takes place with the formation of silver iodide, and a silver salt of an organic acid containing iodine.

On the other hand, Stenhouse[4] has shown that silver-chloranilate, when heated with ethyl iodide, gives an ethyl ether melting at 107°. This substance, which is volatile without decomposition, is extremely stable in the presence of bromine or nitric acid. A chloroform solution of the substance, allowed to stand a long time with an excess of bromine, is not changed. A compound having the formula  must necessarily take up bromine, while a compound, , could not be affected by bromine.

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[1] Hantzsch and Schniter; Ber. d. chem. Ges. **20**, 2040.

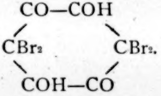
[2] Levy and Jedlicka; Ibid. **20**, 2319.

[3] Levy and Jedlicka; Ibid. **21**, 318.

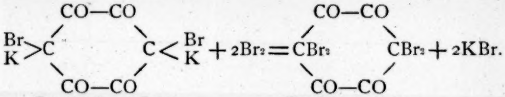
[4] Journ. Lond. R. Soc. Proc. **23**, 4.

The experiments with ethyl chloranilate, and with the salts of chloranilic and nitranilic acid, will be continued. It seems to me that the above facts already make it probable that the anilic acids are para-derivatives of tetra-keto-hexamethylene.

POSTSCRIPT.

A paper by Hantzsch in the Berichte der deutschen chemischen Gesellschaft, Vol. 21, p. 2421, has just been received. By the action of two molecules of bromine in water on potassium bromanilate, Hantzsch has obtained a colorless product to which he has given the formula, 

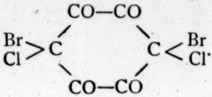
From the results presented in the foregoing paper, it will be evident that the compound cannot possess this formula. The reaction simply takes place as follows:



Potassium bromanilate.

Tetrabrom-tetraketo-hexamethylene.

The so-called bromanilic acid dibrom addition-product is therefore nothing but tetrabrom-tetraketo-hexamethylene.

By the action of two molecules of bromine on potassium chloranilate, I have also obtained a colorless product soluble in ether, which is probably  These facts, as well as the further results presented in Hantzsch's paper, do but confirm the constitution of the anilic acids as being para-derivatives of tetraketo-hexamethylene.

The action of bromine on salts having the metal bound directly to a carbon atom is different in that the bromine takes the place occupied by the metal, *i. e.* substitution takes place. In the other case, where the metal is bound to carbon by means of oxygen, products free from bromine are obtained (see the two foregoing papers).

La Fayette, Ind., *Sept.* 30, 1888.

SEPARATION OF ALUMINIUM AND ZIRCONIUM.

By I. Thomas Davis, Jr.

While studying some of the iodine compounds of zirconium it was found that the iodate, when precipitated from neutral or very feebly acid solutions, gave filtrates in which no zirconium could be detected with ammonia. This apparent insolubility and the fact that aluminium iodate, according to Berzelius,[1] was deliquescent, suggested the possibility of separating these metals by means of an alkaline iodate. Solutions of aluminium refused to show the least signs of precipitation when treated in a manner similar to that by which complete precipitation had been obtained from zirconium salts. In order to examine the method quantitatively, a solution of zirconium chloride in hydrochloric acid was employed. This solution was prepared as follows:

Zircon was decomposed with sodium carbonate and hydrate, the fusion boiled out repeatedly with water, and the residual sodium zirconate decomposed with sulphuric acid. This solution was evaporated carefully to dryness, and kept at a heat just below redness for half an hour. It was then dissolved in water to which a little sulphuric acid had been added, and precipitated with ammonia. The resulting hydrate was dissolved in hydrochloric acid, and the zirconium precipitated several times with sodium thiosulphate, to separate the last trace of iron. The zirconium was finally precipitated with ammonia, washed until the filtrate no longer reacted for chlorine, dissolved in hydrochloric acid, which was added in sufficient quantity to prevent the deposition of an oxychloride, and diluted to the proper strength. It contained in round numbers 5 per cent. of hydrochloric acid by weight.

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[1] Lehrb. ed. 1843-48; **3**, 479.

In order to standardise this solution, the zirconium was precipitated with ammonia, using to a certain extent the same precautions which are to be observed when aluminium is precipitated in a similar manner, and Nos. (1) and (2) represent duplicate determinations.

	Weight of Solution.	ZrO_2 found.	ZrO_2 in 25 grams.
(1)	25.344 grams	.1696 gram	.1673 gram
(2)	25.322	.1686	.1669

The average, .1671 gram, has been taken as representing the correct amount of the tetrachloride, $ZrCl_4$, in terms of the dioxide, ZrO_2, in 25 grams of the solution.

Qualitative experiments seemed to point to the possibility of complete precipitation, as an oxyiodate, when the solution contained a moderate amount of free acid.

	Weight of Solution.	ZrO_2 used.	ZrO_2 found.	Error.
(3)	25.325	.1693	.1604	.0089 —
(4)	25.297	.1691	.1576	.0115 —

In (3) and (4) the acid was neutralised with sodium carbonate, and hydrochloric acid added in such quantity that the solutions contained 1 per cent. by weight. Sodium iodate was then added in excess and the solutions brought to a boil, and fifteen minutes afterwards filtered, washed with hot water until the filtrate and washings in each case amounted to about 400 cc. They were dried and ignited together with the filters. During the ignition slight explosions took place, and once the lid of the crucible, which contained (4), was thrown off. At the same time it took prolonged ignition at the highest heat of the blast-lamp to arrive at constant weight, small quantities of iodine vapors being evolved. These vapors were due to sodium iodate retained by the precipitate, as the zirconium salt seems to part with its iodine at a heat below redness. Hence, the idea of igniting this iodate or of precipitating zirconium from solutions containing much acid was abandoned.

Wts. of Solution.	ZrO_2 used.	ZrO_2 found.	Error.
(5) 20.300	.1357	.1380	.0023+
(6) 20.159	.1347	.1349	.0002+

In (5) and (6) the acid of the zirconium solution was neutralised with sodium carbonate, which was added until a permanent precipitate was formed. This was dissolved in the smallest possible quantity of dilute hydrochloric acid, sodium iodate added in excess, and the solutions boiled for 15 minutes. Instead of filtering immediately, as in (3) and (4), it was thought safest to allow them to stand some time. They were, therefore, allowed to stand over night, then filtered, washed with hot water, dissolved in hydrochloric acid, of which it took a considerable amount, even while hot, precipitated with ammonia, ignited, and weighed. Unfortunately in (5) the washing was very imperfect, but in (6) and all subsequent experiments the washing was continued until the filtrates no longer gave a reaction for chlorine.

Wt. of Solution.	ZrO_2 used.	ZrO_2 found.	Error.
(7) 10.086	.0674	.0674	0
(8) 10.088	.0674	.0682	.0008+
(9) 20.263	.1354	.1352	.0002—
(10) 20.408	.1364	.1365	.0001+

(7), (8), (9), and (10) were carried on exactly like (5) and (6), with the exception that to (9) 5 grams of sodium chloride were added, and to (10) 10 grams. Precipitation seems to be complete, and sodium chloride is without action on the iodate. In filtering the iodate, which is flocculent, it is safest to use Swedish paper, as the precipitate can be more readily washed off without loss than from some of the other papers used.

These experiments having turned out so satisfactorily, it was thought possible that complete precipitation might take place in solutions containing some free acid, but not nearly in such quantity as had been employed in (3) and (4). To determine this point, (11) and (12) were made.

Wt. of Solution.	ZrO_2 used.	ZrO_2 found.	Error.
(11) 30.337	.2028	.1996	.0032—
(12) 30.410	.2032	.2010	.0022—

The acid was neutralised as before, and enough hydrochloric acid added to make the solution contain about 0.1 per cent. of it.

Aluminium chloride was also added in quantity about three times that of the zirconium chloride present. The solution of aluminium chloride was prepared by precipitating pure potassium alum several times to separate all sulphuric acid, and the hydrate dissolved in hydrochloric acid. Its strength was only approximately known. It is evident that precipitation, even in the presence of this small amount of acid, is incomplete. However, no aluminium seems to have been thrown down. The solutions, then, previous to precipitation must be nearly neutral. Therefore, in (13–14) and (15–16) the precipitation was carried on as in (5) and (6).

	Wt. of Solution.	ZrO_2 used.	ZrO_2 found.	Error.
(13)	10.097	.0675	.0673	.0002—
(14)	10.070	.0673	.0671	.0002—
(15)	49.490	.3308	.3302	.0006—
(16)	49.398	.3302	.3301	.0001—

In (13) and (14) the quantity of aluminium was about three times that of the zirconium, while in (15) and (16) equal quantities were used. These numbers seem to be within the error of analysis. Therefore, to separate these two metals, I proceed as follows: Their solution in hydrochloric acid is treated with sodium carbonate until a permanent precipitate is formed. This precipitate is dissolved in the smallest possible quantity of dilute hydrochloric acid, and sodium iodate added in excess. The solution is heated for about fifteen minutes. It is then allowed to stand 12 hours, filtered, washed down with boiling water, dissolved in hydrochloric acid, and finally precipitated with ammonia, ignited, and weighed. A convenient strength of solution is 100 mgs. ZrO_2 in 100 cc.

Three analyses of the zirconium salt proved it to be an oxyiodate of variable composition. Several attempts were made to separate iron, both in the ferrous and ferric state, but without success. This metal must be removed from the mixture of aluminium and zirconium previous to their treatment with sodium iodate.

NOTES OF WORK FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA.

No. XVII.

Communicated by F. P. DUNNINGTON.

143.—EXAMINATION OF A COPPER SLAG OF RED COLOR CONTAINING ARTIFICIAL CUPRITE.

BY J. L. JARMAN AND J. F. MCCALEB.

On a former occasion a specimen of similar slag was examined in this laboratory,[1] when attention was drawn to the pale yellow powder remaining on digestion in aqua regia.

The specimen in hand has been received from the Canton Copper Works of Baltimore, Md., and has been more fully examined, with the following results. It is very hard and tenacious, breaks with conchoidal fracture and knife-like splintery edges, having scattered throughout its mass small spherical cavities and also very minute beads of metallic copper; is opaque, with a dark scarlet color. Sp. grav. = 3.486. H. = 4.8. Analysis of the entire slag affords:

SiO_2	38.039
Cu_2O	47.489
Al_2O_3	2.001
FeO	2.829
CaO	2.525
MgO	.404
K_2O	.549
Na_2O	5.920
	99.756

A thin section of the slag was examined under the microscope and found to consist of a transparent matrix of pale yellow color, in which is closely imbedded minute transparent crystals of cochineal red color, mostly in cubical and rectangular forms, similar to those of common salt, with less distinctly shown octahedra. All of these crystals have a thickness of about .002 millimeter. A portion of the slag was brought to an exceedingly fine powder and digested upon a water-bath with 8 per cent. nitric acid, which removed 46.29 per cent. of its mass, and of this 43.49 per cent. was cuprous oxide. The resulting pale yellow powder showing no red fragments under the microscope, was then digested for two hours in 20 per cent. sodium hydrate, which was found to dissolve but .5 per cent. of silica. From these results we infer that the red color of such slag is due only to cuprous oxide and not to any cuprous silicate; and we note that this cuprous oxide is in the form of native cuprite, similar also to that recently observed by Professor W. G. Brown.[1]

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[1] This Journal **8**, 429.

The pale yellow powder thus prepared, and insoluble both in aqua regia and in sodium hydrate, was further examined with the following results: sp. gr. = 2.31; H. = 4.8; fusible at 2 without change of color, but in the oxidising flame, and more readily when also in a borax bead, it affords a blue glass The analysis gave:

SiO_2	69.22	1000
Al_2O_3	4.84	61
FeO	5.74	70
CaO	3.33	
MgO	.89	
Cu_2O	5.65	92
K_2O	.61	
Na_2O	10.34	
	100.62	

This oxygen ratio suggests petalite, in which the ratio is $\dot{\mathrm{R}} : \dddot{\mathrm{R}} : \mathrm{Si} = 1:4:20$; but in this slag we have $\dot{\mathrm{R}} : \dddot{\mathrm{R}} : \mathrm{Si} = 8:3:50$.

The highly acid nature of this slag is the more remarkable when we recollect that the basic cuprous oxide was distributed throughout the mass, and had, no doubt, separated in crystals from the mass when in a state of fusion.

144.—A COMPARISON OF THE RATES OF SOLUTION OF GYPSUM AND ANHYDRITE.

By J. F. McCaleb.

Both gypsum and anhydrite are employed as fertilisers, but since the former contains 20 per cent. of water, while the latter contains none, it is of economic interest to ascertain whether or not each is to be valued in proportion to the amount of calcium sulphate in it. Both of these bodies are rather insoluble in water, and are employed under conditions which call for solution before any effect is produced.

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[1] Am. J. Sci. **32**, 379.

It was therefore first undertaken to determine the rates of solution by digestion of the powdered substances, but it was soon observed that the flexible crystals of selenite could not with certainty be brought to the same state of subdivision as the harder and more brittle anhydrite, and the rate of solution depended too largely upon the degree of fineness. The experiment was then conducted as follows: A compact lump of each of the several specimens was cut to present some flat surface, and partially covered with paraffin, leaving exposed from 6 to 9 sq. cm. area. Each of these was suspended by a platinum wire, just beneath the surface of four liters of distilled water contained in a tall specie jar. These were allowed to stand undisturbed at a temperature varying from 19° to 23° C. At the end of a week the lumps were temporarily removed, the contents of each jar mixed, and a sample of 100 cc. taken, in which the SO_3 was determined as $BaSO_4$, and from this the $CaSO_4$ was calculated. No specimen of crystallised anhydrite was available. The following specimens were used:

A. Gypsum "pure," pink micaceous mass, Saltville, Va.
B. Gypsum "pure," white massive, Nova Scotia.
C. Selenite "pure," honey-yellow crystal, Montmartre.
D. Anhydrite "impure," grey massive, Salzberg.
E. Anhydrite "pure" (97 per cent.), greyish massive, Nova Scotia.
F. Gypsum and anhydrite mixed, white massive, Nova Scotia.

Amounts of calcium sulphate in grams dissolved from each square centimeter of surface in one week:

A.	B.	C.	D.	E.	F.
.2388	.2219	.1177	.0666	.0601	.2184

The different results from the three hydrated specimens A, B, and C are explained by their respective forms, A being composed of an aggregation of small crystals, which greatly increased the actual surface exposed to the solvent. In B the crystals are minute and more compacted. With C, only a single crystal face (clino-diagonal) was exposed, which was uniformly removed by the solvent.

As to the specimens of anhydrite D and E, D contained of anhydrite about 81 per cent., selenite about 13 per cent., sand and organic matter about 6 per cent.; E contained of anhydrite about 97 per cent.; and we note that the greater solubility of the selenite present in D has given more to the solution than 19 per cent. of anhydrite would have done.

Specimen F, being composed partly of anhydrite and of gypsum, was dissolved irregularly, leaving a rough surface with seams and pits, and clearly showing the varying composition of the surface exposed.

We can best judge of the relative rate of solution of gypsum and anhydrite by comparing the results of B and E, since these were very similar in structure and appearance. From these we infer that, where in powder of the same degree of fineness and in contact with a large amount of water, the anhydrite requires for its solution from three to four-fold the time that the gypsum does.

Continuing these observations, to ascertain something of the action of the solvent as it becomes more nearly saturated, specimens B, C, and D were exposed for a longer time, and afforded the following:

Amounts of calcium sulphate in grams dissolved for each sq. centimeter of surface.

	1 week.	2 weeks.	3 weeks.	4 weeks.	5 weeks.
B	.2219	.4638	.6788	.8168	.8768
C	.1177	.2021	.3250	.4179	.4893
D	.0666	.0999	.1514	.1881	.2398

From the foregoing we note that the ratio between the amounts dissolved from the several specimens during each of the weeks continues about the same. The rate of solution diminished a little as the solvent became more nearly saturated, while the smaller amounts dissolved from all three specimens in the 2d and 4th weeks was probably due to a change of temperature, of which no record was kept. The largest amount dissolved was 5.87 grams from B in five weeks, and equivalent to about 75 per cent. of saturation.

145.—ON THE HYDRATION OF CALCIUM SULPHATE.

By J. F. McCaleb.

In close relation to the preceding article is the problem, At what rate is anhydrous calcium sulphate converted into the hydrate?

Ordinary "Plaster of Paris" will in a few minutes combine with water with which it is mixed; on the other hand, extensive beds of anhydrite are found which have been by long exposure altered, in part, to gypsum. The question then arises: At what rate will this hydration take place with native anhydrite and with different forms of dehydrated gypsum when kept in contact with water?

It was first ascertained that, at common temperature, and over sulphuric acid, all water is taken up from admixture with either hydrated or anhydrous calcium sulphate, while none is removed from chemical combination.

The specimens of anhydrite designated in the preceding article as D and E were employed, and also a specimen, G, obtained by bringing selenite, C, to a bright red heat. One gram of each specimen in fine powder was weighed into a watch-glass, moistened, and kept over water under a bell-jar. From time to time it was found necessary to renew the addition of water to the watch-glass. In order to ascertain the extent of hydration, the watch-glass, with contents, was dried over sulphuric acid and weighed. As the hydrate was formed there was some caking of the powder, which interfered with the regularity of the change which was taking place.

Several watch-glasses, each containing one gram of anhydrite D, were similarly exposed to moisture at temperature 20° to 25° C., and absorbed of water as follows:

Weeks exposed:	4	8	12	16	20	28	36
Water absorbed:	.0308	.0488	.0629	.0700	.0803	.0873	.0949

From which we note that, upon mere digestion with water, where the solution is not removed, the rate of combination is a slow one, gradually diminishing, and under the conditions given would probably be completed in two years.

One gram of each of the three specimens D, E, and G was kept moist at 25° to 30° C. and found to combine with water, as follows:

	1 week.	2 weeks.	3 weeks.
D	.0209	.0357	.0493
E	.0072	.0155	.0234
G	.0022	.0048	.0073

From this it appears that the rate at which the hydration takes place varies greatly with the different specimens, and probably this rate is determined by the extent to which these different specimens have been compacted by the heat which effected their dehydration; for specimen D still retained a small amount of water, and specimen G had been exposed to a bright red heat. To gain some information on the latter point the following investigation was made:

146.—ON THE SPECIFIC GRAVITY OF CALCIUM SULPHATE.

By J. F. McCaleb.

In making these estimations a specific gravity bottle was used, and in order to avoid any hydration of the substances, a paraffin oil having a high boiling point was employed. As this oil expands greatly on being heated, it was found necessary to pay special attention to all changes of temperature and make due corrections.

Most of the following figures are averages of concording results, and all are given with reference to water at 15° C.

1. "Plaster of Paris" obtained by heating crystallised selenite (C) to 200° C., sp. gr. = 2.577.

2. Same selenite heated to dull red, sp. gr. = 2.911.

3. Same selenite heated to bright red, sp. gr. = 2.890.

4. Same selenite heated on platinum, just melted before hot blast blowpipe, sp. gr. = 2.796.

5. Same selenite, in a clay crucible and well luted, was packed within one of graphite and heated in a wind furnace, using gas carbon for fuel. The resulting glassy mass showed numerous minute cavities (no doubt due to escaping gas when in fusion); it gave sp. gr. = 2.654.

6. Anhydrite (E, 97 per cent. pure) massive, sp. gr. = 2.907.

I append from the tables of Professor Clark:[1]

Selenite, sp. gr. = 2.30 to 2.33.
Anhydrite, sp. gr. = 2.92 to 2.98.
$2CaSO_4 + H_2O$, sp. gr. = 2.757.

Comparing the results of experiments 1, 2, and 6, we note that after the water has been expelled, up to a certain point, further heating compacts the aggregation of the molecules of the calcium sulphate until it attains the specific gravity of anhydrite, and in this condition, whether produced in nature or artificially, combination with water takes place very slowly.

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[1] Constants of Nature, Part I, pp. 81, 82.

We note also from 2, 3, 4, and 5 that as the heating is carried beyond a dull red, the specific gravity is diminished; possibly the explanation of this is found in the small cavities seen in 5, which may have been present but microscopic in specimens 3 and 4.

The peculiar hydrate, $2CaSO_4 + H_2O$, mentioned above, was formed within a steam boiler,[1] and probably at a temperature of 150° C. If we imagine this substance to be deprived of its water, without changing the aggregation of the remaining molecules—that is, not altering its volume—its specific gravity would then be $2.757 \times \frac{290 - 18}{290} = 2.585$. This latter figure is practically identical with the specific gravity of plaster of Paris (2.577) as stated above.

Since it has recently been shown by Messrs. Shenstone and Cundall[2] that gypsum may be dehydrated in dry air at 100° C., and even at 70° C., it would be of interest to ascertain what is the specific gravity of the anhydrous calcium sulphates thus produced, and how they compare with the hydrates of calcium sulphate which have been formed under pressure at different temperatures.

147.—ANALYSIS OF OYSTER SHELLS AND OYSTER SHELL LIME.

By L. P. Brown and J. S. H. Koiner.

The sample of shell, retaining the usual small amount of mud, was taken from the dump at a lime-kiln near Baltimore, where the burning of the shell is effected in the following manner. It is fed into a conical brick-lined shaft, together with one-tenth of its bulk of dust of either anthracite or bituminous coal, which latter suffices to maintain the combustion. The specimen of lime was taken immediately from the grate of the kiln, and, of course, contains the ash of the coal dust.

Analysis afforded the following; the result for shell being the average of two independent analyses.

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[1] Johnston, P. M. (2), **13**, 325.

[2] Jour. Chem. Soc. **307**, 544.

	Oyster Shell.	Shell-Lime.
CaO,	52.14	85.49
CO_2,	41.61	.70
MgO,	.25	.31
FeO,	.17	...
Fe_2O_3,	...	.33
Al_2O_3,	.08	.42
Na_2O,	.32	.69
K_2O,	.03	.11
SO_3,	.16	.66
P_2O_5,	.04	.15
Cl,	trace	trace
SiO_2 soluble,	.06	1.14
Insoluble residue,	3.24	5.15
Organic matter,	2.32	...
Nitrogen,	.14	...
Water,	...	3.97
	100.42	99.12

From the former we note, that by present prices the shell contains per ton not more than 50 cents worth of ammonia, which is lost in the burning. This small amount of nitrogen would not warrant the use of any mechanical means of subdivision of the shell, as has been proposed and practised on a small scale. From the latter analysis we see that shell lime compares favorably in purity with the fair grades of stone lime.

148.—ANALYSIS OF "TOBACCO SCREENINGS" REJECTED IN THE MANUFACTURE OF TOBACCO.

By L. P. Brown.

This material consists of the small fragments of stems and leaves which with the dust are sifted from tobacco after it has been ground, in the process of preparing smoking tobacco.

Much of this substance is mixed in certain manufactured fertilisers, and is not unfrequently applied directly as a top-dressing to grass, etc.

The sample examined was taken from a lot of the screenings shipped from Lynchburg, and afforded the following:

Water lost at 100° C.,	10.27
Total (crude) ash,	43.40
Organic matter (by difference),	46.33
	100.

In the Organic Matter.

Nicotine,	.36	
Albumenoids and nitrates,	6.96	
(Total nitrogen) equivalent to ammonia,		1.48

Constituents of the ash:

	In 100 parts of Screenings.	In 100 parts of Ash.
K_2O,	1.187	2.89
Na_2O,	.506	1.23
CaO,	2.796	6.81
MgO,	.346	.84
Al_2O_3,	.192	.47
Fe_2O_3,	.212	.52
SiO_2,	33.760	82.32
P_2O_5,	.296	.72
SO_3,	.483	1.14
Cl,	.451	1.10
SiO_2, soluble,	.907	2.21
Deduct O, equiv. to Cl,	...	.25
	41.136	100.00

In estimating the value of this substance as a fertiliser, we must consider the nicotine, which acts as an insecticide, in addition to the organic matter and the plant food ingredients. As to the latter and the nitrogen, there is contained in 2000 pounds, reckoning at present commercial prices, potash, phosphoric acid, and nitrogen to the value of $6.

149.—ANALYSIS OF A "FIRE EXTINGUISHER."

BY R. A. BAIRD.

From the published analyses of a number of these fire-extinguishing liquids it appears that they are composed essentially of an aqueous solution of one or more of the following bodies: sodium, potassium, ammonium, magnesium, and calcium chlorides and sulphates, and occasionally borax and sodium acetate.

In the examination of a new brand of these articles I found it was composed largely of sodium hyposulphite. As I am not aware that this substance has been mentioned heretofore as being used for this purpose, an analysis of it has been made by Mr. Baird, with the following results: The vessel contained about 5 gills, 600 cc. of solution, in which there were found :

Sodium hyposulphite, . . .	255.55	grams.
Sodium chloride, . . .	48.12	"
Ammonium chloride, . . .	12.60	"
Ammonia, free, . . .	12.24	"
	328.51	

150.—ANALYSIS OF PYROLUSITE FROM CRIMORA MINE, AUGUSTA CO., VA.

By J. L. Jarman.

The ores obtained from this mine have maintained for some years a reputation for peculiar purity, samples from large cargoes showing 79 to 82 per cent. of manganese oxides and over 57 per cent. of metallic manganese. The larger portion of this ore consists of psilomelane mixed with about one-third as much pyrolusite, occurring in nodular masses and distributed through a disintegrated calcareous shale. I have recently received a fine mass of this ore, weighing about fifty pounds, and from it obtained material for the following analysis by Mr. Jarman. It consists of a network of fibrous crystals, closely matted; color, grey; streak, black; H. = 2.7; sp. gr. = 4.69; infusible. Analysis gave :

		Molec. ratio.
MnO, ...	78.270	110.24
O, ...	17.610	110.06
Fe_2O_3, ...	.617	.38
CaO, ...	.094	.18
NiO, ...	.225	.30
CoO, ...	.269	.36
K_2O, ...	.179	.18
Na_2O, ...	.232	.37
H_2O, ...	2.085	1.63
Insol. res., . . .	.293	
	99.874	

Omitting the moisture, this shows the mineral to contain 98 per cent. of MnO_2.

It appears of interest to record this occurrence of pyrolusite of unusual purity from an American locality.

UNIVERSITY OF VIRGINIA, *Sept.*, 1888.

ON THE RELATIVE STABILITY OF THE ALKYL BROMIDES.[1]

BY FELIX LENGFELD.

A short time ago, a careful study of the methods which seemed most likely to lead to satisfactory results in the investigation of the relative stability of the alkyl bromides, was made by Remsen and Hillyer,[2] and it was shown that of all the reactions studied, those with salts of silver and caustic soda were most promising. At the suggestion of Professor Remsen, I have investigated somewhat in detail the decomposition of a number of the alkyl bromides under the influence of sodium and potassium hydroxides, ammonia, silver nitrate, nitric acid, sulphuric acid, and a mixture of silver nitrate and nitric acid, and the results are recorded in this paper.

Substances Used.

As the alkyl bromides used are insoluble in water, the reagents were used in alcoholic solution. They were made as follows:

The solutions of sodic hydrate were made by dissolving sodium in 99.5 per cent. alcohol, and were $\frac{n}{5}$, $\frac{n}{10}$, $\frac{n}{20}$, $\frac{n}{40}$ and $\frac{n}{50}$. They were standardised each time before using.

The solution of potassic hydrate was made in a similar way and was $\frac{n}{10}$.

The solution of ammonia was $\frac{n}{10}$, and was made by dissolving ammonia in 99.5 per cent. alcohol.

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[1] From the Author's Dissertation for the Degree of Doctor of Philosophy at the Johns Hopkins University, 1888.

[2] This Journal **8**, 251.

The solution of silver nitrate, made by dissolving the salt in 85 per cent. alcohol, was $\frac{n}{10}$.

The solution of silver nitrate and nitric acid was made by adding to the silver nitrate solution just described, nitric acid in the proportion of 6.3 grams to the liter.

The solutions of nitric and of sulphuric acids were made by dissolving the acids in 85 per cent. alcohol and were $\frac{n}{10}$.

The bromides used were ethyl bromide, boiling at 38°–39°; propyl bromide, boiling at 70°–71.5°; butyl bromide, boiling at 99°–101°; isopropyl bromide, boiling at 60°–63°; isobutyl bromide, boiling at 92°–93°; isoamyl bromide, boiling at 119°–120°; tertiary butyl bromide, boiling at 71°–73°, and ethylene bromide, boiling at 131.5°–132°. The propyl, isopropyl, isobutyl and isoamyl bromides were prepared from Kahlbaum's by washing with water, drying over calcic chloride, and subjecting to fractional distillation. The ethyl bromide was made by the action of bromine and phosphorus on alcohol, and the ethylene bromide by the action of bromine on ethylene. The butyl bromide was prepared from butyl alcohol made by Lieben and Rossi's method.[1] Instead, however, of making the bromide, as was done by these chemists,[2] by heating the alcohol and hydrobromic acid in a sealed tube, I made it by the action of bromine and red phosphorus on the alcohol. The yield by this method is very poor, only fifteen grams of bromide being obtained from eighty grams of alcohol, whereas Lieben and Rossi obtained one and a half grams of bromide for every gram of alcohol used. The tertiary butyl bromide was made by the action of bromine and red phosphorus on Kahlbaum's trimethyl carbinol, boiling at 83°–86°. The yield was poor, only seven grams of the bromide being obtained from one hundred grams of the alcohol.

The bromides were kept over calcic chloride in the dark. They were tested from time to time to determine whether or not they undergo spontaneous decomposition. The ethyl, propyl, butyl and isopropyl and ethylene bromides showed no evidence of any change. The isobutyl bromide, though at first neutral to test paper and containing no free bromine, contained after two months an amount of hydrobromic acid corresponding to a decomposition of 3.09 per cent. Three weeks later the decomposition had increased to 6.6 per cent., and 1.52 per cent. of the isoamyl bromide had decomposed. Both bromides remained perfectly colorless. Their boiling points had changed but slightly. They were carefully washed, dried, and subjected to fractional distillation. The fractions used were tested and found to contain no impurities, but, after a month, 4.03 per cent. of the isobutyl bromide had again decomposed. The tendency of isobutyl and isoamyl bromides to decompose spontaneously was observed, in alcoholic solutions of these compounds, by Remsen and Hillyer.[1] This property of these bodies throws doubt upon the utility of some of the data obtained from them. I shall call attention to this further on. The tertiary butyl bromide commenced to decompose after a few days. It was therefore, as the quantity was small, put into small bulbs which were sealed and kept in the dark. One of the bulbs was put into a bottle which was tightly corked and the bulb broken, as it seemed desirable to determine the relative amount of decomposition in contact and out of contact with the air. After three and a half months, 63.13 per cent. of that in contact with the air, and 51.99 per cent. of that in a bulb, had decomposed. As bromine, shown by its brown color, and isobutylene are formed in this decomposition, the difference observed may be due to the low "limit" of the decomposition in the bulb (owing to pressure, etc.) rather than to the specific action of the air. Roozeboom[2] noticed that this bromide turns yellow on standing and that its vapor begins to dissociate below 100°. As Eltekoff[3] observed the dissociation of the vapor of isobutyl bromide, it seems probable that the spontaneous decomposition of isobutyl, isoamyl and tertiary butyl bromides is of the same general nature as dissociation.

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[1] Ann. Chem. (Liebig) **158**, 150.

[2] Loc. cit. 161.

As secondary butyl bromide was needed to complete the list of butyl bromides, an attempt was made to prepare it. The method that suggested itself was the action of hydrobromic acid on the alcohol. It was thought that the reduction of ethylmethylketone would give the alcohol, and therefore this ketone was made by heating a mixture of calcium propionate and acetate. All attempts to reduce it to the corresponding alcohol failed. Its alcoholic solution was treated with metallic sodium, and its aqueous solution with sodium amalgam (1 per cent. and 2 per cent.), with zinc and sulphuric acid, and with tin and hydrochloric acid, but the ketone was recovered unchanged. The subject was not pursued further on account of lack of time and a desire to go on with the main investigation. There can be no doubt that the body I attempted to reduce is a ketone, and, though it was not analysed, its boiling point and method of preparation show that it is ethylmethylketone.

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[1] This Journal **8**, 261.

[2] Ber. d. chem. Gesell. **14**, 2396.

[3] Ibid. **8**, 1244.

To determine the stability at low temperatures, the bromides were weighed in sealed bulbs, these put into bottles of about 250 cc. capacity, the solution of the reagent added, the bottles closed with well ground stoppers, the bulbs broken by shaking, the bottles allowed to stand the required time, and, excepting in the first experiments, the amount of bromine extracted determined by Volhard's method. As silver nitrate decomposes the bromides, ferric sulphate and ammonium sulphocyanate were first added and then titrated to disappearance of color. In the experiments at higher temperatures, bottles of 125 cc. capacity were used, and instead of glass stoppers, corks. These were tied down and paraffined. Otherwise the method was the same as at lower temperatures. The use of bulbs prevents loss from volatility of the bromides, and, as the bromide is not brought into contact with the reagent until the bulb is broken, the system may be brought to any desired temperature without any action taking place at a lower temperature. The only apparent disadvantage attending the use of bulbs is the difficulty of putting the same quantity of liquid in every bulb. It therefore seemed desirable to determine if the absolute amount of bromide used has any effect upon the relative amount of decomposition.

INFLUENCE OF QUANTITY OF BROMIDE.

Different quantities of ethyl bromide were dissolved in equivalent quantities of sodic hydrate solution, $\frac{n}{10}$, allowed to stand for the periods of time given below, and the amount of decomposition determined by the loss of alkalinity. The results are as follows:

Time in Hours.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
18.5	.5390	.044145	8.19
18.5	1.0570	.085089	8.05
16.5	.2954	.012208	4.13
16.5	.1430	.005995	4.19
16.5	.2457	.009265	3.77

The first two were not started at the same time as the others, but at a time when the laboratory was much warmer, hence the greater velocity of change. An inspection of these figures shows that though the results do not agree very well, the percentage of change is apparently independent of the quantity of bromide. As the alkaline solution changes on standing, portions of it were put into 250 cc. bottles, allowed to stand a day, and the amount of change found to depend upon the bottle used, not being the same in any two. As, if the amount of bromide decomposed is determined by loss of alkalinity, this difference vitiates the result, even if blanks are used, the direct determination of the bromine abstracted was tried, the method being that given on page 43.

Different quantities of ethyl bromide were dissolved in sodic hydrate, $\frac{n}{10}$, allowed to stand seventy-two hours, and the amount of bromine abstracted determined.

Quantity Used.	Quantity Decomposed.	Percentage of Change.
.7533	.126985	16.85
.4628	.076300	16.48
.6316	.107910	17.07
.3870	.064310	16.61

These results show that the quantity of bromide used is without influence on the percentage of decomposition.

To determine the relative stability of the bromides toward sodic hydrate, at ordinary temperatures, duplicates of each bromide in equivalent quantities of sodic hydrate solution, $\frac{n}{10}$, were allowed to stand for the periods given below.

RELATIVE STABILITY TOWARD SODIC HYDRATE.

Series I.

This series was allowed to stand one day.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.2788	.051775	18.57
Ethyl,	.24225	.042946	17.72
Propyl,	.2688	.018327	6.82
Propyl,	.3298	.023739	7.19

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Butyl,	.2345	.014933	6.38
Butyl,	.2459	.015755	6.40
Isopropyl,	.2514	.004428	1.76
Isopropyl,	.3115	.004920	1.58
Isobutyl,	.23365	.005257	2.25
Isobutyl,	.2740	.008055	2.94
Isoamyl,	.3508	.012835	3.66
Isoamyl,	.2714	.010419	3.58
Ethylene,	.2040	.089206	43.73
Ethylene,	.1721	.075294	43.75
Tertiary butyl,	.1832	.15618	85.25

Series II.

This series was allowed to stand two days. As one of the bottles containing ethyl bromide was cracked in breaking the bulb, but one determination of ethyl bromide was made.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.2469	.070959	28.74
Propyl,	.1654	.020418	12.34
Propyl,	.2769	.036531	13.19
Butyl,	.2131	.023975	11.25
Butyl,	.2020	.023016	11.39
Isopropyl,	.2200	.007011	3.19
Isopropyl,	.2212	.007011	3.17
Isobutyl,	.2182	.009274	4.25
Isobutyl,	.2247	.009348	4.16
Isoamyl,	.26015	.011627	4.47
Isoamyl,	.2442	.012684	5.19
Ethylene,	.1711	.084318	49.30
Ethylene,	.1833	.090240	49.23
Tertiary butyl,	.1315	.114943	87.41

Series III.

This series was allowed to stand four days. Only a single determination of ethyl bromide is given, as one of the bottles was accidentally broken.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.2141	.081401	38.02
Propyl,	.1610	.033456	20.78
Propyl,	.1527	.031857	20.86
Butyl,	.1235	.022331	18.08
Butyl,	.1889	.035072	18.56
Isopropyl,	.1784	.008610	4.87
Isopropyl,	.1988	.009592	4.81
Isobutyl,	.2050	.011615	5.75
Isobutyl,	.1866	.010674	5.72
Isoamyl,	.1985	.017969	9.04
Isoamyl,	.2087	.019026	9.11
Ethylene,	.1917	.097290	50.75
Ethylene,	.1444	.073320	50.77
Tertiary butyl,	.1309	.118505	87.94

Series IV.

This series was allowed to stand seven days. During this period the temperature of the laboratory ranged from zero to 25°.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.5021	.232715	46.34
Ethyl,	.4847	.226185	46.66
Propyl,	.3648	.083025	22.75
Propyl,	.3378	.075645	22.39
Butyl,	.2786	.055211	19.80
Butyl,	.3520	.071788	20.39
Isopropyl,	.2725	.017712	6.50
Isopropyl,	.3551	.023001	6.47
Isobutyl,	.3231	.029866	9.24
Isobutyl,	.4699	.043840	9.32
Isoamyl,	.4341	.045300	10.43
Isoamyl,	.3740	.039160	10.46
Ethylene,	.4319	.223720	51.10
Ethylene,	.5206	.266020	51.09
Tertiary butyl,	.2173	.191800	88.27

Series V.

This series was allowed to stand fourteen days. The range of temperature was about the same as in Series IV.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.2005	.138757	69.20
Ethyl,	.1473	.101588	68.96
Propyl,	.2473	.106026	42.87
Propyl,	.2462	.105780	42.96
Butyl,	.2172	.078638	36.20
Butyl,	.2148	.082200	38.22
Isopropyl,	.2192	.032964	15.08
Isopropyl,	.1720	.028290	16.04
Isobutyl,	.2006	.035620	17.76
Isobutyl,	.2209	.038360	17.37
Isoamyl,	.2949	.063420	21.50
Isoamyl,	.2629	.058739	22.38
Ethylene,	.3711	.190820	51.42
Ethylene,	.4447	.228420	51.36
Tertiary butyl,	.1695	.157139	92.70

Series VI.

This series was allowed to stand twenty-eight days. The range of temperature was the same as in Series IV and V.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.4251	.346947	81.61
Ethyl,	.1819	.146823	80.71
Propyl,	.2066	.121647	58.85
Propyl,	.4224	.251781	59.60
Butyl,	.2688	.147275	54.78
Butyl,	.2227	.122752	55.11
Isopropyl,	.2616	.059778	22.85
Isopropyl,	.3579	.079335	22.17
Isobutyl,	.4309	.106723	24.76
Isobutyl,	.3791	.092886	24.50
Isoamyl,	.3021	.096187	31.83
Isoamyl,	.3583	.119592	33.87
Ethylene,	.5117	.266720	52.13
Ethylene,	.3221	.167252	51.92
Tertiary butyl,	.1697	.151248	89.12

Series VII.

This series was allowed to stand sixty-three days. Only one determination of each bromide was made.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.1882	.167315	88.90
Propyl,	.3914	.296922	75.86
Butyl,	.2667	.190841	71.59
Isopropyl,	.3784	.146493	38.71
Isobutyl,	.4443	.174812	39.34
Isoamyl,	.3254	.160513	49.35
Ethylene,	.3625	.189410	52.28

In order to render a comparison of these results as easy as possible, I have gathered them into one table which I have put on the following page. The figures at the heads of the columns indicate the time in days, and the results are given in per cents. Wherever two determinations were made their mean is given.

Summary.

Bromide.	1 day.	2 days.	4 days.	7 days.	14 days.	28 days.	63 days.
Ethyl,	18.14	28.74	38.02	46.50	69.08	81.16	88.96
Propyl,	7.00	12.71	20.82	22.57	42.91	59.18	75.86
Butyl,	6.39	11.32	18.32	20.10	37.21	54.93	71.59
Isopropyl,	1.67	3.18	4.84	6.48	15.60	22.51	38.71
Isobutyl,	2.60	4.20	5.74	9.28	17.57	24.63	39.34
Isoamyl,	3.62	4.83	9.08	10.45	21.89	31.85	49.35
Ethylene,	43.74	49.27	50.76	51.09	51.39	52.02	52.28
Tertiary butyl,	85.25	87.41	87.94	88.27	92.70	89.12	not determined.

We notice that up to a certain point, peculiar to each, ethylene and tertiary butyl bromides decompose very rapidly, but that as soon as this point is reached the decomposition proceeds very slowly. As the decomposition, however, progresses beyond this point, the phenomenon can scarcely be due to the establishment of equilibrium between the reacting bodies and the products of the reaction. It appears more probable that these bromides are entirely decomposed, and that other organic bromides, difficultly decomposable, are among the products. This view is strengthened by the fact that the "critical" point in the case of the ethylene bromide is the point at which half the bromine has been abstracted by the sodic hydrate. This corresponds to the formation of vinyl bromide, $C_2H_4Br_2 + NaOH = C_2H_3Br + NaBr + H_2O$; and Wislicenus[1] has shown the stability of vinyl compounds. The decomposition of the other bromides appears to be normal and regular. Their relative stability is, in order of increasing stability, ethyl, propyl, butyl, isoamyl, isobutyl, and isopropyl. To determine if this order of stability remains constant with increasing concentration, suitable quantities of the bromides were dissolved in $\frac{n}{5}$ sodic hydrate solution, and allowed to stand at the temperature of the laboratory one, two and four days.

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[1] Annalen **212**, 246.

Series VIII.

This series was allowed to stand one day.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3962	.136359	34.42
Propyl,	.4732	.056949	15.20
Butyl,	.3841	.041100	10.70
Isopropyl,	.5122	.013898	2.69
Isobutyl,	.5575	.022300	4.00
Isoamyl,	.5094	.028841	5.66
Ethylene,	.2816	.136278	48.39
Tertiary butyl,	.2489	.209610	84.21

Series IX.

This series was allowed to stand two days.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3484	.150747	43.27
Propyl,	.4589	.096678	21.06
Butyl,	.2672	.051238	19.17
Isopropyl,	.3699	.018849	5.09
Isobutyl,	.4281	.025772	6.02
Isoamyl,	.3906	.035089	8.98
Ethylene,	.2621	.132258	50.45
Tertiary butyl,	.2349	.200842	85.54

Series X.

This series was allowed to stand four days.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3286	.190602	58.00
Propyl,	.3829	.124476	32.50
Butyl,	.2567	.075213	29.30
Isopropyl,	.3320	.028167	8.48
Isobutyl,	.3885	.036287	9.34
Isoamyl,	.3672	.053209	14.49
Ethylene,	.2341	.120602	51.51
Tertiary butyl,	.2437	.214268	87.94

Leaving ethylene bromide, for reasons already given, out of consideration, we see that the relative stability is not affected by changing the concentration of the solutions. We find that the isobromides are more stable toward sodic hydrate than the normal bromides, which in turn are, if we may draw any conclusion from the one example studied, more stable than the tertiary bromides. Isopropyl bromide, a secondary bromide, is the most stable of those investigated. On trying to find the connection between the formulæ and the relative stability of the bromides, we see that the group $(CH_3)_2\overset{|}{C}H$ apparently exerts a restraining influence on the bromine. The bromides containing this group are comparatively stable. Comparing their formulæ, $(CH_3)_2CHCH_2CH_2Br$, $(CH_3)_2CHCH_2Br$ and $(CH_3)_2CHBr$, we observe that as the bromine "approaches" the "protecting" group it becomes more fixed. Further investigation of the subject is required before it can be stated that the group $(CH_3)_2\overset{|}{C}H$ does really "protect" the bromine. The action of other reagents seems to indicate that it does not, but that we have here merely a coincidence.

Comparing stability and molecular weight, we find that the stability of normal bromides increases while that of isobromides decreases with increasing molecular weight.

Having now determined the relative stability toward sodic hydrate, the action of other reagents was tried. The solutions of ammonia, potassic hydrate, nitric acid, sulphuric acid and silver nitrate described on pages 40 and 41 were used.

ACTION OF AMMONIA.

The first experiments upon the action of ammonia were made by heating to 60° for one hour, but, owing to pressure, several of the bottles broke and the series is incomplete.

Series XI.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3080	.005450	1.77
Propyl,	.2716	.003444	1.27
Isopropyl,	.3397	.000861	.25

The experiments were therefore repeated at zero. The series was allowed to stand one hundred and forty-five hours in a vessel containing melting ice. The results obtained are as follows:

Series XII.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.7544	.002834	.37
Propyl,	.7039	.002091	.29
Isopropyl,	.7106	.000246	.034
Isobutyl,	.5358	.022742	4.22[1]
Isoamyl,	.6643	.008909	1.34
Ethylene,	.4418	.000188	.042

The amount of change was determined by estimating by Volhard's method the quantity of bromine abstracted, and, as the products of the reaction are ammonium bromide and alkyl ammonium bromides, it became necessary to ascertain if the latter hold their bromine in such a way that it can be determined by this method. Investigation proved that the bromine is so held. This and the slowness of action of ammonia on alkyl bromides indicate a re-arrangement in the formation of alkyl ammonium bromides, and are opposed to the view that these are molecular compounds, for were they molecular compounds they would be formed quite rapidly and the bromine combined in the same way as in the alkyl bromides, and not capable of determination by Volhard's method.

ACTION OF POTASSIC HYDRATE.

These experiments were made by allowing the solutions to stand at zero for one hundred and forty-five hours.

Series XIII.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.7920	.137040	17.29
Propyl,	.7299	.046740	6.40
Isopropyl,	.8881	.011193	1.26
Isobutyl,	.4765	.026304	5.52[1]
Isoamyl,	.5599	.019781	3.53
Ethylene,	.4442	.185180	41.68

These results show that the order of stability toward potassic hydrate is the same as toward sodic hydrate. As a series[2] of experiments upon the action of sodic hydrate at zero was undertaken at the same time as Series XII and XIII, I have thought it desirable to compare the percentage results obtained. At the top of each column is the name of the alkali used.

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[1] 4.03 per cent. due to spontaneous decomposition.

[2] Series XVIII.

Comparison of Results.

Bromide.	Sodic Hydrate.	Potassic Hydrate.	Ammonia.
Ethyl,	15.20	17.28	.37
Propyl,	7.02	6.40	.29
Isopropyl,	1.44	1.26	.034
Isobutyl,	1.65[1]	1.49[1]	.19[1]
Isoamyl,	3.86	3.53	1.34
Ethylene,	40.96	41.68	.042

We see that the ratio between the action of these alkalies on the bromides is not constant, but depends upon the bromide used. As Ostwald has shown that this ratio, in the case of bases acting upon acids, is independent of the acid used, it is probable that the variability noticed above is due to secondary action. It shows that the reactions between alkyl bromides and alkalies are not applicable to determinations of the relative affinity of bases. Reicher[2] obtained similar results on comparing the action of sodic and baric hydrates on acetic ethers, as the coefficients thus obtained do not bear a constant ratio to each other. Ammonia acts very slowly on the bromides. Its action upon ethylene bromide is particularly striking, as, compared with sodic or potassic hydrate, it decomposes but one one-thousandth as much of this compound, which, unstable toward the others, is very stable toward it. The comparatively great decomposition of the isoamyl bromide may be due to the instability of its solutions. This source of error was determined in the case of the isobutyl bromide, and the figures given in the table have been corrected. In the experiments upon the action of potassic hydrate and ammonia, butyl and tertiary butyl bromides were omitted, as the quantity of each at my disposal was small and needed for other experiments.

ACTION OF ACIDS.

Preliminary experiments having shown that the bromides are decomposed very slowly by nitric and sulphuric acids at ordinary temperatures, the solutions, after standing eight days at the temperature of the laboratory, were heated to 60° for twelve hours.

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[1] Corrected.

[2] Ann. Chem. (Liebig) **232**, 106.

ACTION OF NITRIC ACID.

Series XIV.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3375	.082513	24.48
Propyl,	.2817	.035793	12.70
Butyl,	.1714	.017810	10.39
Isopropyl,	.2408	.054858	22.78
Isobutyl,	.3043	.017536	5.76
Isoamyl,	.2865	.028539	9.96
Ethylene,	.3109	.001692	.54
Tertiary butyl,	.1646	.106723	64.84

ACTION OF SULPHURIC ACID.

Series XV.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3977	.086437	21.73
Propyl,	.2079	.021156	10.17
Butyl,	.2083	.021641	10.38
Isopropyl,	.2673	.075030	28.06
Isobutyl,	.1656	.009179	5.54
Isoamyl,	.4436	.039411	8.88
Ethylene,	.3274	.001880	.57

We see that the relative stability toward acids is not the same as toward bases. Ethylene bromide, so unstable with potassic and sodic hydrates, is hardly attacked by acids ; and isopropyl bromide, so stable with alkalies, is, when treated with nitric acid, the most unstable of the bromides, and is easily attacked by sulphuric acid. With nitric acid, as with alkalies, the relative stability of normal bromides increases and that of primary isobromides decreases with increasing molecular weight. With sulphuric acid, however, propyl bromide is more stable than butyl bromide, but the difference is very slight and may be due to experimental error. The action of nitric and sulphuric acids upon the alkyl bromides is complicated by their action upon the alcoholic solvent. To determine the extent of this secondary action, vials containing some of the acid solutions were treated in the same way as Series XIV and XV and the loss of acidity determined. This amounted to 5.88 per cent. in the nitric acid and 24 per cent. in the sulphuric.

ACTION OF SILVER NITRATE.

Silver nitrate, both in neutral and in acid solution, was allowed to act upon the bromides. The solutions were kept in the dark twenty-two hours and the unchanged silver nitrate determined.

Series XVI.

Bromide.	Qnantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3874	.187698	48.68
Propyl,	.3138	.106146	33.82
Butyl,	.2541	.082474	32.45
Isopropyl,	.2451	.228919	92.99
Isobutyl,	.3030	.028907	9.54
Isoamyl,	.2522	.065987	26.16
Ethylene,	.2813	.005076	1.80

With silver nitrate, as with acids, ethylene bromide is very stable and isopropyl bromide very unstable. Compared with other reagents, silver nitrate acts rapidly on most of the bromides. The order of stability of ethyl, propyl, butyl, isobutyl, and isoamyl bromides is the same as toward nitric acid and sodic and potassic hydrates.

ACTION OF SILVER NITRATE AND NITRIC ACID.

To determine the action of silver nitrate in acid solution, the solution of silver nitrate and nitric acid described on page 41 was used. The conditions were the same as in Series XVI.

Series XVII.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.2363	.123606	52.30
Propyl,	.2940	.132963	45.19
Isopropyl,	.3728	.368016	98.71
Isobutyl,	.3301	.036990	11.17
Isoamyl,	.3421	.098602	28.81
Ethylene,	.2845	.006298	2.21

The order of stability is the same as in neutral solution, but the amount of change is in all cases greater. As the action of nitric acid alone, under the same conditions, is almost inappreciable (less than .1 per cent.), the increased amount of change cannot be due to its specific action upon the alkyl bromides, but indicates the increased activity of silver nitrate in acid solution.

INFLUENCE OF TEMPERATURE.

The influence of temperature on chemical action, though universally recognised since the time of Bergmann, forms, as Ostwald says, "the subject of one of the darkest chapters in chemical mechanics." Wilhelmy, in 1850, attempted to give a mathematical expression for the influence of temperature on the velocity of a reaction. Since then Berthelot,[1] Harcourt and Esson,[2] Warder,[3] and Hood[4] have proposed formulæ, but they are applicable only to special cases. Van't Hoff[5] and Reicher[6] have applied a formula proposed by the former, and found the results calculated to agree with those obtained. Urech[7] has deduced and applied a formula differing slightly from that of Van't Hoff. All the chemists mentioned, as well as Fleurie,[8] Ostwald,[9] Menschutkin,[10] and Sabatier,[11] have studied the subject experimentally, but, though many interesting facts have been brought to light by this happy combination of theory and experiment, we are still far from the goal, and it will probably be many years before we have a general formula for expressing the influence of temperature on all chemical reactions. Van't Hoff[12] has indeed said that "the influence of temperature on the velocity of change depends upon the reaction chosen for consideration"; and Ostwald,[13] in his work on the action of acids on acetamide, found that the ratio between the velocity coefficients at 65° and at 100° varies with the acid used. Urech[14] observed similar phenomena in studying the inversion coefficients of acids. It was therefore considered necessary to study the influence of temperature upon the stability of the alkyl bromides, in order to determine if the variations are sufficient to change the order of stability. The reaction with sodic hydrate was chosen for this purpose. A $\frac{n}{10}$ solution was used throughout and, as in the experiments at ordinary temperatures, the bromides were dissolved in equivalent quantities of this solution.

To determine the influence of temperature it is necessary to compare the so-called "velocity coefficients." As is readily seen, the ratio between the amounts changed at two temperatures in one hour will differ from the corresponding ratio in two hours. For if in one hour at the temperature t 50 per cent. of the compound used is decomposed, and at the temperature t' 10 per cent., in the next hour 50 per cent. and 10 per cent. respectively of the remainders will be decomposed, and therefore in two hours 75 per cent. and 19 per cent. The ratios are in one hour 50 : 10 or 5 : 1, and in two hours 75 : 19 or about 4 : 1. Therefore some function must be compared which is independent of the time chosen. The velocity of a chemical change depends, other things being equal, upon the quantities of the reacting bodies and upon a constant which is a function of the nature of these bodies. This may be expressed in an irreversible reaction by the equation

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[1] Ann. chim. phys. [3], 68.

[2] J. Chem. Soc. **20**, 492.

[3] This Journal **3**, 347.

[4] Phil. Mag. [5], 6.

[5] Etudes de dynamique chimique, 112.

[6] Ann. Chem. (Liebig) **232**, 113.

[7] Ber. d. chem. Gesell. **16**, 762.

[8] Ann. chim. phys. [5], **7**, 391.

[9] J. prakt. Chem. [2], **27**, 26.

[10] Ibid. [2], **29**, 437.

[11] C. R. **106**, 63.

[12] Etudes de dynamique chimique, 117.

[13] J. prakt. Chem. [2], **27**, 26.

[14] Ber. d. chem. Gesell. **16**, 762.

$$\frac{dx}{dt} = K(A-x)(B-x),$$

in which K represents the constant, or velocity coefficient, A and B the molecular quantities of the reagents a and b, and x the amount of change. As, if we use equivalent quantities of a and b, A and B become equal, we may write the equation $\frac{dx}{dt} = K(A-x)^2$. Integrating we get, as t and x reduce to zero together, $\frac{x}{A-x} = AKt$. As this formula can be applied only to irreversible reactions, it became necessary to prove that the reaction studied is not a reversible reaction. For this purpose the action of sodic bromide upon methyl, ethyl, propyl and amyl alcohols and ethylene glycol was studied. Sodic bromide, in the proportions of 10.3 grams and 103 grams to the liter, was heated with the alcohols themselves, with the alcohols to which ten per cent. of water had been added, and with dilute solutions of the alcohols in ethyl alcohol, with and without the addition of ether. Though heated in all these cases to 60° for twenty-four hours, the sodic bromide was not changed. The reaction, therefore, is not reversible. I have therefore used the equation $\frac{x}{A-x} = AKt$ to determine the value of K. The figures thus obtained show what the relative change would be if the "active masses" of the reagents could be kept constant throughout the reaction. They are inversely as the relative time required for the same amount of decomposition. As the figures are comparative, I have, in order to avoid small fractions, multiplied K by one hundred million. A has been chosen equal to one hundred. An ordinary water-bath was used in the preliminary experiments, but, as the temperatures of different parts were different, it was discarded. A drying oven with double walls, the space between being filled with water, was tried and discarded for the same reason. A water-bath of ten liters capacity, placed within a larger bath, was found to have the same temperature throughout and was therefore used. By means of a thermo-regulator the temperature of this bath could be kept constant to within two tenths of a degree. In the experiments at zero the bottles were entirely surrounded by water in which melting ice was kept. In the experiments at other temperatures they were allowed to float upon the hot water, and, as they were never full, about one third was above the surface of the water. Of course the pressure in the bottles varied with the temperature, but the velocity of reactions of this nature was found by Van't Hoff[1] and Berthelot[2] to be independent of the pressure.

STABILITY AT ZERO.

Series XVIII.

This series was kept at zero for one hundred and forty-five hours, hence t, which is the time expressed in minutes, is equal to eight thousand seven hundred.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.	*AKt.*	*K.*
Ethyl,	.7299	.110962	15.20	.17924	20.6
Propyl,	.4184	.029397	7.02	.07550	8.68
Isopropyl,	.8188	.011808	1.44	.01461	1.68
Isobutyl,[3]	.5644	.009313	1.65	.01678	1.93
Isoamyl,	.7931	.030653	3.86	.04017	4.62
Ethylene,	.6101	.249946	40.96	.69376	79.7

STABILITY AT 30°.

Series XIX.

This series was heated to 30°. Duplicates of each bromide were used, one being heated for two hours, the other for three. In the column marked t I have given the time, in minutes, of each determination.

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[1] Etudes, 43.

[2] Ann. chim. phys. [3] **66**, 45.

[3] Tests applied immediately after starting this series showed that the isobutyl bromide had undergone partial decomposition. Therefore the result obtained was corrected and is given as corrected. As with my apparatus I could not keep a temperature between zero and thirty degrees constant, the next experiments were carried on at the latter temperature.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.	*AKt.*	*t.*	*K.*
Ethyl,	.3556	.026375	7.41	.08003	120	667
Ethyl,	.3315	.035643	10.75	.12044	180	668
Propyl,	.2588	.007011	2.71	.02785	120	232
Propyl,	.2772	.011088	4.00	.04166	180	233
Butyl,	.2865	.006166	2.15	.02197	120	183
Butyl,	.1777	.005691	3.20	.03306	180	184
Isopropyl,	.2254	.001728	.77	.00776	120	64
Isopropyl,	.2258	.002683	1.18	.01193	180	66
Ethylene,	.3395	.098408	28.98	.40805	120	3400
Ethylene,	.2452	.087591	35.74	.55742	180	3098

Excepting in the case of ethylene bromide, the duplicates agree so closely that there can be no doubt of the correctness of the formula used. Ethylene bromide acts abnormally.

STABILITY AT 40°.

Series XX.

This series was kept at 40°. Duplicates of each bromide were used, one being heated about one hour, the other about two. As two bottles, one containing ethylene, the other tertiary butyl bromide, were broken, but one determination of each of these bromides was made.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.	*AKt.*	*t.*	*K.*
Ethyl,	.3564	.033459	9.38	.10351	61	1697
Ethyl,	.3166	.054173	17.11	.20642	121	1706
Propyl,	.2049	.007503	3.66	.03799	60	623
Propyl,	.3030	.021402	7.06	.07596	120	627
Butyl,	.1975	.006165	3.12	.03220	61	528
Butyl,	.2116	.013152	6.21	.06621	122	542
Isopropyl,	.3708	.003690	.995	.01005	61	164
Isopropyl,	.2501	.004620	1.967	.02007	121	165
Isoamyl,	.2744	.005436	1.98	.02020	64	315
Isoamyl,	.3279	.011174	3.42	.03541	120	295
Ethylene,	.1541	.043710	33.85	.51156	60	8526
Tertiary butyl,	.1291	.125903	83.42	5.10873	60	85145

STABILITY AT 50°.

Series XXI.

This series was kept at 50°. Duplicates of each bromide were used, as in Series XX. Owing to the breaking of three bottles, one of which contained butyl bromide, and the others isobutyl and tertiary butyl, the series is incomplete.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.	*AKt.*	*t.*	*K.*
Ethyl,	.1940	.043382	22.36	.28799	60	4800
Ethyl,	.2979	.110428	37.03	.58805	120	4900
Propyl,	.2699	.027183	10.07	.11197	60	1866
Propyl,	.2572	.045510	17.69	.21735	120	1811
Butyl,	.2067	.018632	9.01	.09901	60	1650
Isopropyl,	.2205	.006888	3.13	.03231	60	539
Isopropyl,	.3381	.020910	6.18	.06481	120	540
Isobutyl,	.2712	.021697	8.00	.08695	120	725
Isoamyl,	.3103	.017063	5.49	.05703	60	951
Isoamyl,	.2780	.028690	10.32	.11507	120	959
Ethylene,	.3138	.152562	48.61	.94590	60	15766
Ethylene,	.2009	.100837	50.09	1.00360	120	8363
Tertiary butyl,	.1272	.109874	86.38	6.34214	60	105702

STABILITY AT 60°.

Series XXII.

This series was kept at 60° for one hour.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.	*AKt.*	*K.*
Ethyl,	.4232	.184428	43.57	.77210	12868
Propyl,	.3868	.094956	24.55	.32538	5423
Isopropyl,	.2985	.026076	8.73	.09565	1594
Isobutyl,	.2260	.023534	10.41	.11619	1936
Isoamyl,	.3476	.039864	11.46	.12943	2157
Ethylene,	.2421	.123892	51.17	1.04792	17465

The results obtained in Series XVIII to XXII show that the order of stability of the alkyl bromides is the same at all temperatures between zero and 60°. In order that the influence of temperature upon the velocities of the reactions studied may be more readily seen, I have brought all the results into one table, below. The figures given are the values of the velocity coefficient *K*.

Summary.

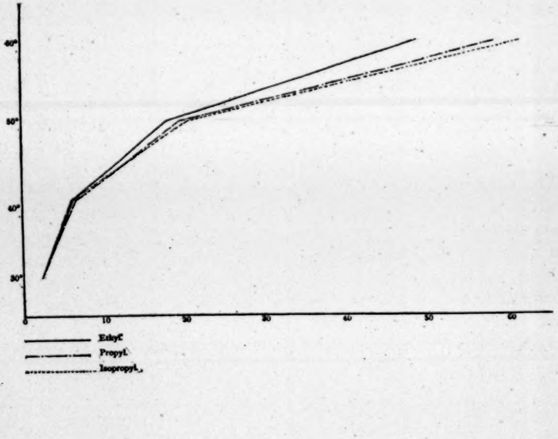
Bromide.	Zero.	30°.	40°.	50°.	60°.
Ethyl,	20.6	667	1702	4850	12868
Propyl,	8.68	232	625	1838	5423
Butyl,	...	183	535	1650	...
Isopropyl,	1.68	65	164	539	1594
Isobutyl,	1.93	...	...	725	1936
Isoamyl,	4.62	...	305	955	2157
Ethylene.	79.7	3551	8526	15766	17465
Tertiary butyl,	...	...	85155	105702	...

The figures obtained for ethylene are not the true values of K, as the reaction between sodic hydrate and ethylene bromide is not regular and normal. It is impossible at present to deduce the true values of K for this reaction. The same is probably true of tertiary butyl bromide. Comparing the velocity coefficients at 30°, 40°, 50°, and 60° with each other, we find that their ratios are, in the case of ethyl bromide, 1 : 2.55 : 7.27 : 19.44 ; in the case of propyl bromide, 1 : 2.69 : 7.92 : 23.37 ; and in the case of isopropyl bromide, 1 : 2.52 : 8.29 : 24.52.

These ratios, though showing a general resemblance, prove the truth of Van't Hoff's statement that "the influence of temperature varies with the reaction under consideration."

Interpolation formulæ of the general form $x = A + at - bt^2 + ct^3$ seem best adapted to express these results. Representing by U the velocity coefficients of the reaction between ethyl bromide and sodic hydrate, by V those of the reaction between propyl bromide and sodic hydrate, and by Z those of the reaction between isopropyl bromide and sodic hydrate, we get the following formulæ:

$$U = 667 + 92.824\theta - 3.702\theta^2 + .4758\theta^3.$$
$$V = 232 + 49.801\theta - 3.642\theta^2 + .2583\theta^3.$$
$$Z = 65 + 8.522\theta - .637\theta^2 + .0672\theta^3.$$
$$\theta = t - 30.$$



These formulæ can be applied only between 30° and 60°. Other formulæ are probably required for other ranges of temperature. The results obtained are graphically expressed by the foregoing cut. To admit of more easy comparison I have divided the velocity coefficients of ethyl bromide by 266.8, of propyl bromide by 92.8, and of isopropyl bromide by 26.

INFLUENCE OF LIGHT.

As the influence of light upon the velocity of reactions of this nature has never been studied, a series of the bromides in $\frac{n}{10}$ sodic hydrate was protected from light, but otherwise kept under the same conditions as Series VI, both being started at the same time.

Series XXIII.

This series was kept, in the dark, twenty-eight days.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.	Series VI.
Ethyl,	.2052	.167533	81.64	81.16
Propyl,	.2646	.158793	60.01	59.23
Butyl,	.3383	.186868	55.23	54.95
Isopropyl,	.3838	.081180	21.24	22.51
Isobutyl,	.2294	.057225	24.93	24.63
Isoamyl,	.4067	.133786	32.89	32.60
Ethylene,	.2175	.111202	51.12	52.02
Tertiary butyl,	.2065	.182758	88.49	89.12

I have put the results of Series VI in the last column. A comparison of this with the fourth column shows that light has no influence on the velocity of reactions of this nature.

EFFECT OF CONCENTRATION.

The velocity of a reaction between two bodies depends, if other conditions remain constant, upon the frequency of impact of the molecules, and therefore, theoretically, the amount of change in unit time is, in unit volume, as the square of the concentration, and, in unit mass, directly as the concentration. From this it follows that the amount of change referred to unit mass is the same in N hours in a solution of concentration C as in one hour in a solution of concentration NC. Van't Hoff[1] and Ostwald[2] found that these theoretical deductions hold good only if very dilute solutions are used, and that the extent to which the dilution must be carried varies with the reaction under consideration. The following experiments were therefore undertaken to determine how far the dilution must be carried in the reactions between sodic hydrate and alkyl bromides. The bromides were dissolved in $\frac{n}{10}$, $\frac{n}{20}$, $\frac{n}{40}$ and $\frac{n}{50}$ sodic hydrate solutions, which were then kept at 54° for one, two, four and five hours respectively.

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[1] Etudes, 25.

[2] J. prakt. Chem. [2] **31**, 307.

Series XXIV.

This series was kept at 54° for one hour. The solutions were $\frac{n}{10}$.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3063	.089698	29.28
Propyl,	.3014	.044526	14.77
Isopropyl,	.3522	.024477	6.95
Ethylene,	.3103	.152374	49.10

Series XXV.

This series was kept at 54° for two hours. The solutions were $\frac{n}{20}$.

Ethyl,	.2710	.090841	33.52
Propyl,	.2942	.053628	18.22
Isopropyl,	.2635	.019922	7.55
Ethylene,	.3644	.181702	49.86

Series XXVI.

This series was kept at 54° for four hours. The solutions were $\frac{n}{40}$.

Ethyl,	.2018	.081751	40.51
Propyl,	.3638	.072570	19.94
Isopropyl,	.4090	.039606	9.68
Ethylene,	.2805	.150964	53.82

Series XXVII.

This series was kept at 54° for five hours. The solutions were $\frac{n}{50}$.

Ethyl,	.2522	.101697	40.32
Propyl,	.2661	.054120	20.33
Isopropyl,	.2600	.024354	9.33
Ethylene,	.2880	.154348	53.82

Bringing the results of Series XXIV to XXVII together in one table, we get the following

Summary.

Bromide.	$\frac{n}{10}$ for one hour.	$\frac{n}{20}$ for two hours.	$\frac{n}{40}$ for four hours.	$\frac{n}{50}$ for five hours.
Ethyl,	29.28	33.52	40.51	40.32
Propyl,	14.77	18.22	19.94	20.33
Isopropyl,	6.95	7.55	9.68	9.33
Ethylene,	49.10	49.86	53.82	53.82

The differences between the figures in the last two columns are within the limit of experimental error; therefore, for dilutions beyond $\frac{n}{40}$ the velocity of change is inversely as the concentration.

INFLUENCE OF SOLVENT.

The specific influence of so-called "neutral" solvents was first noticed by Berthelot and Péan de St. Gilles,[1] who found that the velocity of etherification is less if ether is used as a solvent than if benzene is employed. Ostwald[2] found that the velocity of the action of acids on methyl acetate varies with the solvent, and Menschutkin,[3] in studying the velocity of etherification of alcohols by acetic anhydride, arrived at a similar conclusion. Ostwald used as solvents water, acetone, and methyl and ethyl alcohols; Menschutkin, benzene, hexane and xylene. I therefore thought it desirable to determine the effect of change of solvent upon the velocities of the reactions under consideration. For this purpose $\frac{n}{10}$ solutions of sodic hydrate were made by dissolving metallic sodium in methyl and propyl alcohols, containing about half a per cent. of water. Suitable quantities of the bromides were dissolved in these and the solutions kept at 54° for one hour. As Series XXIV was kept at the same temperature for the same length of time, the results thus obtained admit of comparison with the results of that series.

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[1] Ann. chim. phys. [3], **66**, 66. [2] J. prakt. Chem. [2], **28**, 457. [3] Zeits. phys. Chem. **1**, 628.

Series XXVIII.

In this series the bromides were dissolved in equivalent quantities of $\frac{n}{10}$ solution of sodic hydrate in methyl alcohol. The series was kept at 54° for one hour.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3523	.059514	16.89
Propyl,	.2923	.023004	7.87
Butyl,	.2740	.021235	7.74
Isopropyl,	.3580	.010086	2.81
Ethylene,	.2971	.144760	48.72

Series XXIX.

In this series the bromides were dissolved in equivalent quantities of $\frac{n}{10}$ solution of sodic hydrate in propyl alcohol. The series was kept at 54° for one hour.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.2492	.061149	24.53
Propyl,	.2583	.027180	10.52
Butyl,	.3049	.030825	10.11
Isopropyl,	.3251	.013653	4.19
Ethylene,	.3067	.150588	49.09

Summary.

Bromide.	Methyl Alcohol.	Ethyl Alcohol.	Propyl Alcohol.
Ethyl,	16.89	29.28	24.53
Propyl,	7.87	14.77	10.52
Butyl,	7.74	14.01	10.11
Isopropyl,	2.81	6.95	4.19
Ethylene,	48.72	49.10	49.09

An inspection of this summary shows that the action is slower in methyl alcohol than in propyl alcohol, and slower in propyl alcohol than in ethyl alcohol. As part of the change may be expressed by the equation, $C_nH_{2n+1}Br + NaOH + C_mH_{2m+1}OH = C_nH_{2n+1}OC_mH_{2m+1} + NaBr + H_2O$, it remains an open question whether or not the "active" part taken by the alcohols in this reaction is the cause of the difference in velocity. The influence of the alcohols upon the rate of change does not bear a simple relation to their molecular weights, as the results obtained with propyl alcohol are intermediate between those obtained with methyl and ethyl alcohols as solvents.

EFFECT OF EXCESS OF REAGENT.

According to one of Guldberg and Waage's fundamental equations, $\frac{dx}{dt} = K(nA - x)(mB - x)$, the velocity of a reaction is similarly affected by a similar excess of either reagent. Urech,[1] in his studies on the action of Fehling's solution and dextrose, and of acetyl bromide and bromine, and Landolt,[2] in studying the reaction of sulphurous acid on iodic acid, found that an excess of one reagent produces a different effect on the velocity, from that produced by an excess of the other. Reicher,[3] in his researches on the saponification of ethyl acetate by sodic hydrate, and Hood, in his work on the oxidation of ferrous sulphate by potassic chlorate, found that a similar excess of either reagent has the same effect on the velocity. I have studied the effect of excess of reagent upon the reaction between sodic hydrate and ethyl bromide, using an excess of each reagent under similar conditions, so that the results admit of direct comparison. They are as follows:

Series XXX.

In this series, which was kept at 53° for one hour, ethyl bromide, in $\frac{n}{10}$ solution, was treated with one half, one, two and three equivalents of sodic hydrate.

	Quantity Used.	Quantity Decomposed.	Percentage of Change.	$NaOH : C_2H_5Br$.
Ethyl bromide,	.5501	.186764	15.77	½ : 1
" "	.5207	.146387	28.11	1 : 1
" "	.3023	.135923	44.96	2 : 1
" "	.2514	.141700	56.36	3 : 1

Series XXXI.

In this series, which, like Series XXX, was kept at 53° for one hour, sodic hydrate, in $\frac{n}{10}$ solution, was treated with one half, one, two and three equivalents of ethyl bromide.

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[1] Berichte **17**, **18**, **19**.

[2] Berichte **19**, 1317.

[3] Annalen **228**, 257; and **232**, 103.

	Quantity Used.	Quantity Decomposed.	Percentage of Change.	C_2H_5Br : NaOH.
Sodic hydrate,	.2046	.032286	15.78	½ : 1
" "	.1910	.053691	28.11	1 : 1
" "	.2039	.090777	44.52	2 : 1
" "	.1287	.072124	56.04	3 : 1

The differences in the fourth columns fall within the limit of experimental error, and we may therefore conclude that in this reaction similar effects are produced by similar excess of either reagent.

Comparing all the results obtained, we see that toward sodic or potassic hydrate, nitric acid, silver nitrate, or silver nitrate and nitric acid, the stability of normal bromides increases, and that of primary isobromides decreases, with increasing molecular weight. This order of stability is probably the same toward all reagents, as the slight deviation from it when sulphuric acid is used falls within the limit of error, and the apparent instability of isoamyl bromide toward ammonia is probably due to spontaneous decomposition. We may therefore conclude that that factor of the stability which is a function of the molecular weight is constant with all reagents. This is not true of that factor which is a function of the constitution. Secondary propyl bromide is more stable toward alkalies, but less stable toward other reagents, than the primary bromide. The dibromide studied is less stable toward fixed alkalies than the monobromides, but more stable toward other reagents. As the order of stability of isopropyl, isobutyl, and isoamyl bromides varies with the reagent, and as, excepting with alkalies, isoamyl bromide occupies the intermediate position, it follows that the group $H\overset{|}{C}(CH_3)_2$ exerts its influence only upon the alkalies, or that the "protection" noticed is merely a coincidence. Further investigation is needed to decide this question. Though the spontaneous decomposition of tertiary butyl bromide prevents any great value being attached to the data obtained for the action of reagents on this compound, there can be no doubt that this bromide is very unstable toward alkalies.

JOHNS HOPKINS UNIVERSITY, *June*, 1888.

REVIEWS AND REPORTS.

On Raoult's Method for the Determination of Molecular Weights.

As is well known, the need of a method for determining the molecular weights of compounds which cannot be converted into vapor has long been felt. Such a method appears now to be at our disposal in that proposed by Raoult,[1] which is based upon observations on the depression of the freezing point of solvents by substances in solution. In view of the importance of the method to chemistry, it appears that a brief account of the investigations bearing upon it may be of interest and profit to the readers of this Journal, and accordingly the following paper has been prepared at the suggestion of the editor.

Although published by Raoult in 1883, and in a number of subsequent papers quite fully developed, the method referred to did not attract the attention of chemists generally until the present year. In February last, Victor Meyer,[2] in an article calling attention to its value, characterised it as the most significant contribution to the list of physical processes applicable to chemical investigations since the discovery of the law of Dulong and Petit. This statement, based upon an investigation carried on in his laboratory by Auwers[3] to determine the value and limitations of the method, resulted in arousing the chemical world to its importance. Since then a number of investigators have applied it to various problems of interest, with such success that confidence in its accuracy has rapidly increased, until it may now fairly be said to have taken a permanent place in chemistry.

As early as 1788, Blagden[4] investigated the effect of dissolved salts upon the freezing point of water, and found that the depression was proportional to the concentration of the solution. In 1861, Rüdorff[5] rediscovered this principle, and specially investigating some apparent deviations from the law, found that these could be explained on the assumption of the formation of hydrates, and deduced a formula for determining whether in any solution of a given salt, hydrates are formed, and the amount of water thus combining with the dissolved substance. Ten years later, Coppet,[6] using solutions containing salts dissolved in quantities proportional to their molecular weights, discovered that

[1] Ann. chim. phys. [5] **20, 28**, [6] **2, 4, 8**; Compt. rend. **94, 95, 97, 101, 102, 103, 104**; Ztschr. phys. Chem. **1**, 186.

[2] Ber. d. chem. Ges. **21**, 536.

[3] Ber. d. chem. Ges. **21**, 701.

[4] Phil. Trans. Lond. 1788, p. 277.

[5] Ann. der Phys. Pogg. **114**, 63; **116**, 55; **145**, 599.

[6] Ann. chim. phys. [4] **28**, 366; **25**, 502; **26**, 98.

salts of analogous constitution produced the same depression of the freezing point. In 1883, Raoult[1] investigated the application of this law to solutions of a large number of organic substances in water, with remarkable results. Dividing the observed depression of the freezing point for each substance by the weight dissolved in 100 grams of water, he obtained a coefficient of depression which, multiplied by the molecular weight of the substance as obtained by other methods, gave approximately the same quantity. This constant he termed the molecular depression. If C represent the depression in degrees centigrade, P the number of grams of substance dissolved in 100 grams of water, and M the molecular weight of the substance,

$\frac{C}{P} = A$, the coefficient of depression of the substance, and

$MA = T$, the molecular depression of the solvent.

T is constant not only for solutions of different concentration, but also has approximately the same value for all substances of analogous structure in the same solvent. Raoult therefore proposed to make use of this constant in determining the molecular weight of substances to which the vapor-density methods are not applicable. With a view to developing and perfecting this method, he carried on a series of experiments,[2] using other solvents, as benzene, nitrobenzene, ethylene bromide, formic acid, glacial acetic acid, thymol, and naphthalene, for each of which a different value was found for T. Comparing these values, he found that the depression caused by one molecule of any substance dissolved in 100 molecules of either solvent was very nearly constant, varying between 0.59° and 0.65°, the mean being 0.63°.

In this general form, however, the law is not applicable to the determination of molecular weights. Some solutions give depressions of the freezing point which seem to indicate that the molecules of the substance are doubled in solution; others show irregularities which must be accounted for by assuming partial dissociation. If, however, the molecular depression caused in a given solvent by a substance of known molecular weight is determined, this constant may be used in determining the molecular weight of any substance of similar composition, from the observed depression which it causes in the freezing point of the same solvent. The results thus obtained show a maximum variation of 10 per cent. from the accepted molecular weight, while in most cases the agreement is much closer; so that by observing proper precautions[3] in the application of this method, it can lead to no error in choosing between the multiples of the empirical formula.

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[1] Ann. chim. phys. [5] **28**, 133.

[2] Ann. chim. phys. [6] **2**.

[3] V. Meyer, Ber. d. chem. Ges. **21**, 536; Auwers, same, p. 701.

Of the solvents used,[1] only water, benzene, and acetic acid can find general application. The molecular depression varies greatly for different classes of substances, so that its use is to be avoided where the substance to be examined is soluble in either of the other solvents. It is, however, possible, by properly determining the value of T which should be used, to secure accurate results with water. Benzene, though showing more uniform values of T, gives quite irregular results with some organic compounds containing the group OH. Acetic acid is the only solvent in which T has but one value for all substances, ranging between 36 and 40, with a mean value of 39. The following values of T have been carefully worked out by Raoult:

Water	19.	Most organic substances.
	35.	Salts of monovalent metals with monobasic acids.
	40.	" " " " dibasic "
	45.	Salts of divalent metals with strong monobasic acids.
	17.	" " " " dibasic acids.
Benzene	25.	Alcohols, acids, phenols.
	49.	Other organic compounds.
Acetic acid (glacial)	39.	All substances.

In no case should a solvent be chosen which can enter into chemical union with the substance to be examined.

The application of the method presents no serious difficulties and calls for no special skill in manipulation. The apparatus required is ready at hand in most laboratories. Except in the study of those substances which exhibit variations of the general law, very satisfactory work may be done with a thermometer graduated to tenths of a degree, a large test-tube and a beaker. Of the forms of apparatus described by recent investigators,[2] perhaps the most satisfactory is that proposed by Beckman[3] and shown (slightly modified) in the cut. A small battery-jar *A* is provided with a loosely fitting cover having a small hole *B* near the edge, through which passes a rod or stout wire *C*, bent at the lower extremity into a horizontal ring, to be used in stirring the freezing mixture. In the centre of the cover a large test-tube *D* is fastened, providing an air-space between the freezing mixture and the vessel containing the solvent. *E* is a test-tube having a capacity of about 25 cc. below the large side neck *F*, which serves for the introduction of the substances to be examined. Through the cork in *E*, in addition to the thermometer, a stout platinum wire works closely but freely. At the lower end this is bent into a horizontal ring for stirring. The thermometer, graduated to $\frac{1}{10}$ or $\frac{1}{20}$ degrees, is read with the aid of a lens or cathetometer, and estimated to hundredths of a degree.

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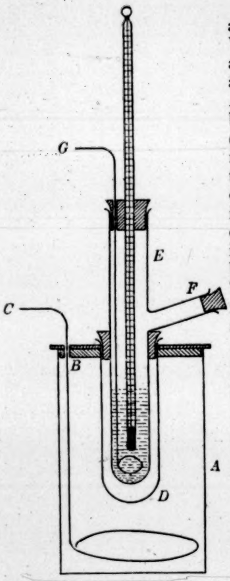
[1] Raoult, Ann. chim. phys. [6] **8**, 320; Paternò, Ber. d. chem. Ges. **21**, 3178; Beckman, Ztschr. phys. Chem. **2**, 715.

[2] Auwers, Ber. d. chem. Ges. **21**, 701; Ramsay, J. Chem. Soc. **54**, 621; Halleman, Ber. d. chem. Ges. **21**, 860.

[3] Ztschr. phys. Chem. **2**, 639.



To make a determination, tare *E*, and put in about 15 cc. of the solvent. Weigh to within a centigram. Put in a few small clippings of platinum foil, adjust the thermometer and insert in *B*. Cool down to half a degree or more below the freezing point of the solvent (as little below as possible will yield more accurate results), and by rubbing the platinum wire against the sharp edges of the foil, crystallisation is set up in the supersaturated liquid. The addition of a small crystal of the solvent is more often used for this purpose, but is less convenient and accurate. The thermometer rapidly rises, and within a few seconds becomes stationary, and remains so for a short time. As soon as this maximum is reached, the thermometer is read. Remove *E*, and thaw by placing in lukewarm water. Freeze again, and repeat until constant results are obtained. The second and third readings should not vary more than 0.02°, and if so, the last may be taken as the freezing point of the solvent. A weighed portion of the substance to be examined is then introduced, and the temperature read as before. Several successive portions may be introduced, increasing the concentration to any desired amount, and the molecular weight indicated at the various degrees of concentration may be calculated from the formula,

$$\text{Molecular weight} = \text{constant}\ \frac{\text{per cent. of substance in solution}}{\text{depression of freezing point}}.$$

The following examples will serve to illustrate the agreement of such results :

Glacial acetic acid.			Water.			Benzene.		
Per cent. of solution.	Depression.	Molecular weight.	Per cent. of solution.	Depression.	Molecular weight.	Per cent. of solution.	Depression.	Molecular weight.
Acetone$(CH_3)_2CO = 58$.			Acetone$(CH_3)_2CO = 58$.			Acetone$(CH_3)_2CO = 58$.		
0.502	0.340	57.6	0.662	0.220	56.9	0.473	0.405	57.2
1.776	1.175	58.9	2.416	0.770	59.3	1.458	1.220	58.6
4.402	2.835	60.6	6.221	1.930	60.9	4.592	3.615	62.2
9.202	5.785	62.0	12.35	3.820	61.1	7.162	5.365	65.4
12.48	7.775	62.8	18.52	5.660	61.8	12.27	8.470	71.0
15.91	9.740	63.7						

The more concentrated the solution the greater the depression, and therefore the less proportionate effect of an error in reading the thermometer. On the other hand, the separation of the first crystals of the solvent in freezing, has, in concentrated solutions, a greater proportionate effect upon the concentration of the remainder, and prevents so great a rise in temperature upon freezing as would occur without this change in concentration; moreover, with a high degree of concentration the liquid must be cooled too far below its freezing point before crystallisation will begin. As a rule, an amount of substance in solution which will cause a depression of from one to two degrees has been found to give the most accurate results. This depends, however, upon the molecular depression of the solvent and the solubility of the substance examined.

With these precautions, it will be found possible to secure reliable results with substances which obey the general law. For those which show a coefficient of depression varying notably with the concentration of the solution, the work of Raoult and Beckman should be consulted.

A summary of some work of Brown and Morris[1] to determine the molecular weight of the carbohydrate raffinose, will convey a better notion of the value of the method. To determine whether the action of substances of this class in aqueous solution is normal, experiments were made with other carbohydrates, the molecular depression being taken at 19, as found by Raoult for organic substances in water.

		Calculated.	Mean found.
Dextrose,	$C_6H_{12}O_6$	180	180.2
Cane sugar,	$C_{12}H_{22}O_{11}$	342	337.5
" " after inversion,			174.3
Maltose,	$C_{12}H_{22}O_{11}$	342	322
Milk sugar,	$C_{12}H_{22}O_{11}$	342	345
Arabinose,	$C_5H_{10}O_5$	150	150.3

Having thus established the value of *T* for these compounds, raffinose was examined, with the following results:

Calculated for $C_{18}H_{32}O_{16}.5H_2O$.	Found mean.
594	528

indicating that the simplest empirical formula, and not a multiple of it, represents the true molecular weight.

Other recently published investigations bearing upon this method are the following: Raffinose, by Tollens and Meyer, Ber. d. chem. Ges. **21**, 1566; Oxides of nitrogen, by Ramsay, J. Chem. Soc. **54**, 621; Sulphur, bromine, iodine and phosphorus, by Paternò and Nasini, Ber. d. chem. Ges. **21**, 2153; Citraconic acid, by the same, Ber. d. chem. Ges. **21**, 2156; Fumaric and maleïc acids, by the same, Ibid.; Aluminium ethyl, by Roux and Louise, Compt. rend. **107**, 600, and Bull. soc. chim. Paris, **50**, 497; Nitriles, by E. von Meyer, J. prak. Chem. N. F. **38**, 339; On the method in general, by Arrhenius, Ztschr. phys. Chem. **2**, 491; and by Hentschel, Ibid. **2**, 306.

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[1] J. Chem. Soc. **54**, 610.

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NOTE.

The Atomic Weight of Tin.

Bongartz and Classen[1] have recently made a redetermination of the atomic weight of tin. They used four methods:

1. Oxidation of metallic tin by nitric acid;
2. Electrolysis of the salt $SnCl_4.2NH_4Cl$;
3. Electrolysis of the salt $SnCl_4.2KCl$;
4. Electrolysis of stannic bromide, $SnBr_4$.

Pure tin was made by starting with the purest Banca tin. This was converted into the tetrachloride, which was carefully fractionated. The pure liquid was treated with enough crystallised sodium sulphide to redissolve all the precipitated stannic sulphide, and after adding a quantity of a solution of pure sodium hydroxide equal to half the sodium sulphide used, and allowing to stand for a few days, the resulting liquid was subjected to electrolysis, when the tin was deposited as a silvery metallic powder. The tin thus prepared was found to be free from antimony. It was converted into the tetrachloride, and to this enough ammonium and potassium chlorides added to form the crystallised double salts, $SnCl_4.2NH_4Cl$ and $SnCl_4.2KCl$. These were carefully and frequently recrystallised. Another part of the tin was converted into the tetrabromide, and this fractionally distilled until pure. The results obtained by the four methods above mentioned are as follows:

By 1. Mean of 11 determinations, Sn = 118.7606;
By 2. " " 16 " Sn = 118.8093;
By 3. " " 10 " Sn = 118.7975;
By 4. " " 10 " Sn = 118.7309.

The 47 determinations give the mean value, Sn = 118.7745, with a difference between the maximum and minimum of 0.2485. The authors consider the results of methods 2 and 3 the most reliable, and the mean result of these gives, as the atomic weight of tin, Sn = 118.8034, which they adopt.

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[1] Ber. d. chem. Gesell. **21**, 2900.